CATALYST DEACTIVATION AND REGENERATION ANALYSIS BY XPS TECHNIQUE.

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The various catalytic systems using XPS techniques studied for the topic are as follows:

I.   *Coke deposited on Ni/HZSM-5 in bio-oil hydro deoxygenation*

Bio-oils produced by fast pyrolysis must undergo hydro deoxygenation as they have high content of oxygen and water making them unfit for transportation purposes. But, due to the hydrocarbon processing, undesired carbonaceous materials are produced and get deposited on the catalyst surface after reactions leading to catalyst deactivation. Ni/zeolite Socony Mobil-Five (Ni/HZSM-5) catalysts are used for the purpose, due to their effectiveness, scalability and stability.

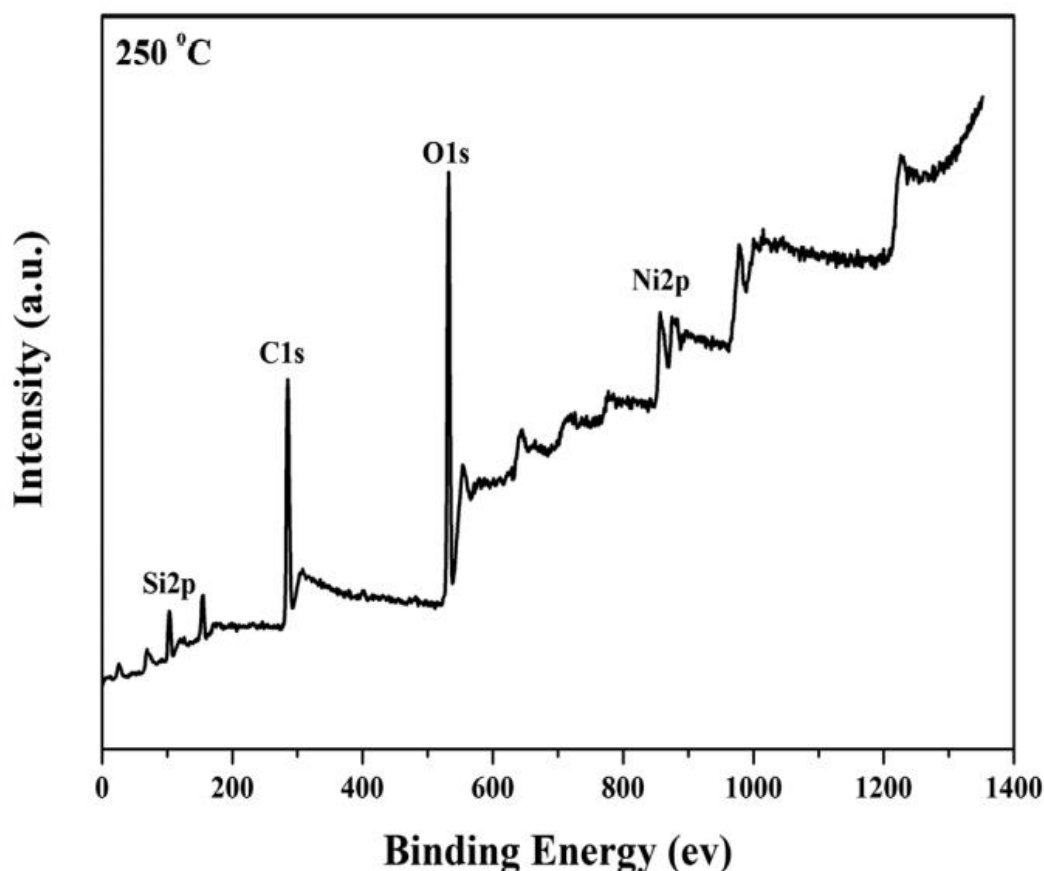***X-ray photoelectron spectroscopy (XPS) analysis of spent catalyst remained after bio-oil HDO:***

Figure 1: Wide scans of XPS Spectra for the spent Ni/HZSM-5 catalyst samples at 250°C.

Observation (Figure 1):

- Silicon, nickel, oxygen and carbon elements are present on the catalyst surface. Oxygen present in the air got adsorbed onto the spent catalyst surface due to the atmospheric exposure.
- Si and Ni found on the upper surface, show that coke deposition on the Ni/HZSM-5 catalyst after bio-oil HDO at varying temperatures is not uniform. The surface of the catalyst is not fully covered by coke.
- Ni and Si signal intensities decrease as reaction temperature increases from 250 to 330°C, and lower Ni and Si signals are found for sample at 300 °C than those found at 250°C, indicating more of the catalytic surface getting covered by coke with increasing reaction temperature.
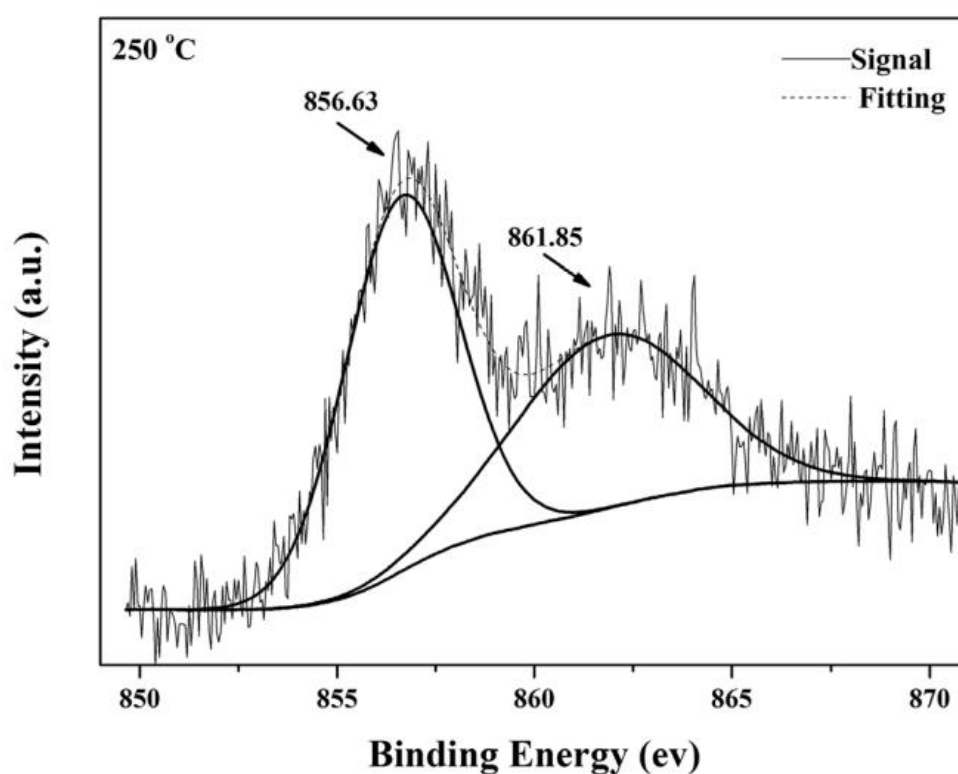

Figure 2: XPS profile of Ni 2p at 250°C for the surface of the spent Ni/HZSM-5 catalyst sample.

Observation (Figure 2):

- The Ni 2p3/2 spectral region for the spent samples has major peak at 856.6 eV for sample at 250°C and at 857.2 eV at 300°C.
- The difference in value is attributable to adsorbed oxygen on the surface. Binding energy increases during transition from metallic environment to an insulating one, reducing screening from metallic to dielectric, which explains the observed shift.
- The satellite lines serve as a proof of the presence of nickel ions in oxide ion environment. The second component of Ni 2p3/2 at 861.9 for the sample at 250°C.

Nickel ions interact with zeolite lattice, silicon and oxygen, so the traces of nickel silicate exist, but the amount for the same on the surface decreases quickly with increasing temperature. With

increasing reaction temperature, Ni 2p spectra peak intensities decline, indicating a decline in Ni/HZSM-5 catalyst surface area due to greater levels of coke deposition.

Conclusion:

XPS basically indicates that the area containing Ni becomes covered by coke with increasing reaction temperature. Carbon compounds containing oxygen serve as the main constituents of coke deposited. With increasing temperature, soluble carbon gets converted to insoluble ones, increasing the number of hard carbon compounds which undergo polymerization or polycondensation and lead to main coke forming reaction.

II.   *Deactivation and Regeneration for the SO$_2$-Poisoning of a Cu-SSZ-13 Catalyst in the NH$_3$-SCR Reaction*

Cu-SSZ-13, the predominant commercial selective catalytic reduction (SCR) catalyst in the NH$_3$-SCR reaction is used widely because of its superior activity and durability. However, SCR catalysts readily undergo hydrothermal aging and sulphur poisoning. SO$_2$ poisoning influences the chabazite (CHA) structure that even regeneration cannot restore its original structure, the redox ability and ammonia storage performance also getting influenced by sulfation and the regeneration process. Various reversible and irreversible damage such as dealumination of the framework structure, accumulation and distribution of different state copper species occur due to sulfur poisoning. Also, the extent of decrease in redox ability is more.

Evaluation of the surface characteristics of catalysts in fresh, sulphated and regenerated states by X-ray photoelectron spectroscopy (XPS):

According to literature:

- Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks ascribed to Cu^{2+} appeared at about 933.3 and 955.5 eV, with two shakeup satellite peaks located at about 939.9 and 944.7 eV.
- Peaks assigned to Cu$^+$ species are located at about 932.4 and 952.6 eV.
- Peak at around 938.3 eV pertained to Cu^{2+} in CuO, and the one at 944.1 eV represented the existence of dispersed Cu^{2+} species on the surface.

Observation (Figure 3):

- In comparison with the fresh Cu-SSZ-13, the amount of Cu^{2+}, Cu$^+$, Cu^{2+} in CuO and dispersed Cu^{2+} species decreased significantly after sulfur treatment, indicating a great loss of surface Cu species in the catalyst.
- Appreciable decrease existed for the regenerated catalyst, suggesting that the loss of surface copper species was irreversible.
- Ratio of Cu$^+$/Cu^{2+}, calculated by the area ratio of corresponding peaks came highest for fresh catalyst F-Cu (0.89), demonstrating that more Cu+ existed on the surface of the fresh sample; the same ratio decreased on the surface of the sulfured and regenerated samples.
- Ratio of Cu$^+$/Cu^{2+} increased with regeneration temperature rising and reached to the maximum (0.84) for R-650 (i.e. Regeneration at 650°C), demonstrating that high

temperature regeneration can achieve removal of sulfur species and formation of Cu^+ species. While the amount of Cu+ ions decreased with the temperature increasing to 700°C.
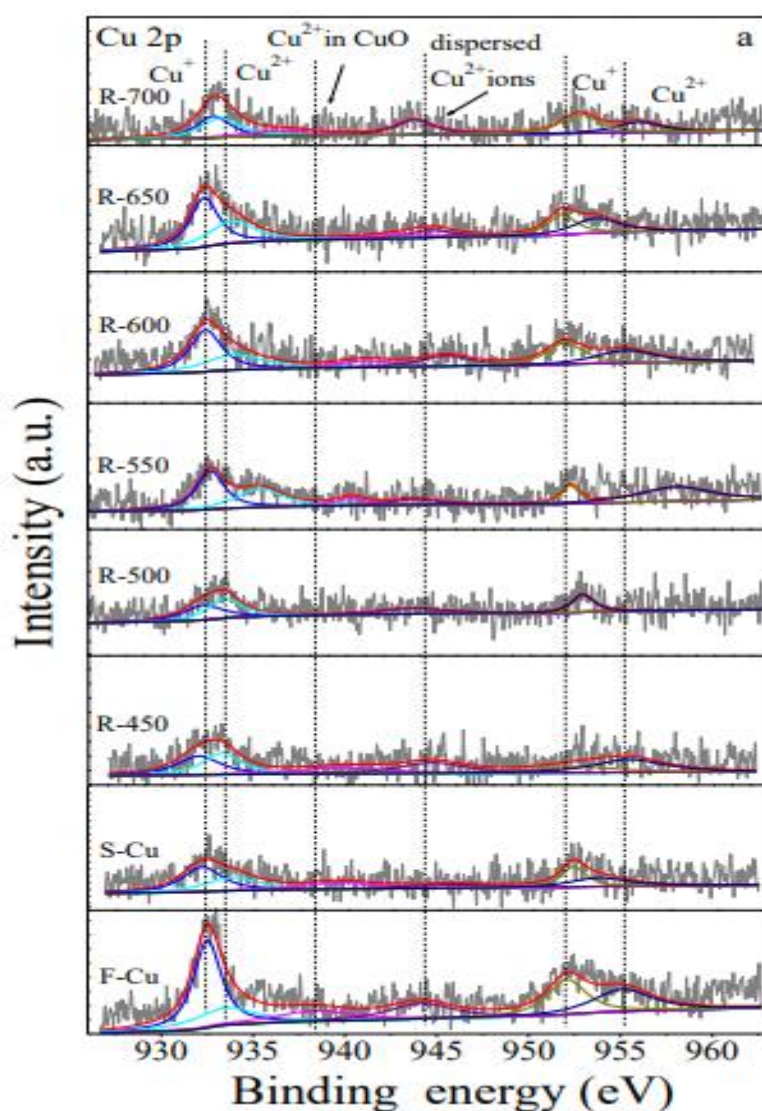

Figure 3: Cu 2p X-ray photoelectron spectra (XPS) spectra of Cu-SSZ-13 catalysts in fresh, sulfated and regenerated state.

The XPS spectra of S 2p:

- Peak at about 169.2 eV in S 2p spectra corresponds to signal of SO_4^{2-} demonstrating the presence of sulfur species on both of the sulfated and regenerated state catalysts.
- No SO_3^{2-} species on poisoned catalysts surface because of the presence of excessive O_2 during sulfating process.
- After regeneration process, the amount of sulfur complexes decreased monotonically with increasing temperature, and the sulfur species vanished when the regeneration temperature reached 700°C.
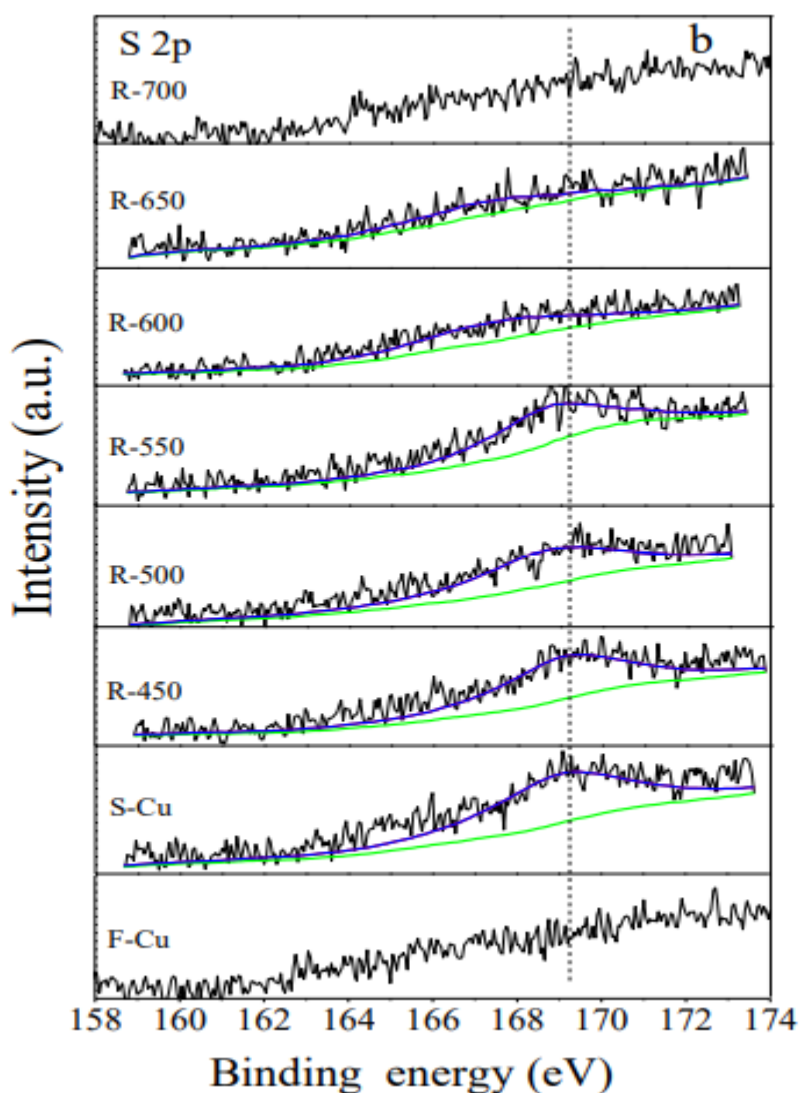
Figure 4: S 2p X-ray photoelectron spectra (XPS) spectra of Cu-SSZ-13 catalysts in fresh, sulfated and regenerated state.

Conclusion:

XPS results reveal that despite, the possible formation of $CuSO_4$ or H_2SO_4 due to reaction of SO_2 with H_2O and O_2 on the Cu-SSZ-13 catalysts, the bonding strength between surface Cu (Cu^{2+}, Cu^+ or Cu^+/H^+) and S remains so weak that it gets broken in the regeneration process. Thus, the SCR activity of the Cu-SSZ-13 catalyst recovers well after the regeneration at 700°C. But for the optimal performance of the catalyst, it must not exceed the regeneration temperature of 650°C, as intensity from Cu 2p spectra gained is greater at 650°C than at 700°C.

III. *Deactivation and regeneration of Pt/TiO2 nanosheet-type catalysts with exposed (0 0 1) facets.*

Formaldehyde is one of the major indoor air pollutants and can cause many health issues. HCHO can be completely decomposed into CO_2 and H_2O on Pt/TiO_2 catalysts at room temperature. The disadvantage of the catalyst is deactivation or poisoning. Pt- supported

catalysts generally undergo deactivation due to Cl, S, CO, SO_2 etc. F-poisoning/deactivation phenomenon is reported for a Pt/TiO_2-NS catalyst during the HCHO oxidative decomposition at room temperature, and an efficient regeneration method of the deactivated catalysts is proposed by NaOH washing resulting in the removal of remaining fluorine easily from TiO_2 surface.

Three samples taken for the XPS analysis are:

Sample A: F-poisoned/deactivated Pt/FTiO_2-NS catalyst prepared by impregnation of as-prepared FTiO_2-NS with Pt precursor followed by reduction with $NaBH_4$.

Sample B: Obtained by washing sample A with NaOH solution.

Sample C: F-free Pt/TiO_2-NS catalyst prepared using F-free TiO_2-NS.

Evaluation of the surface characteristics of the three samples of catalyst by X-ray photoelectron spectroscopy (XPS):
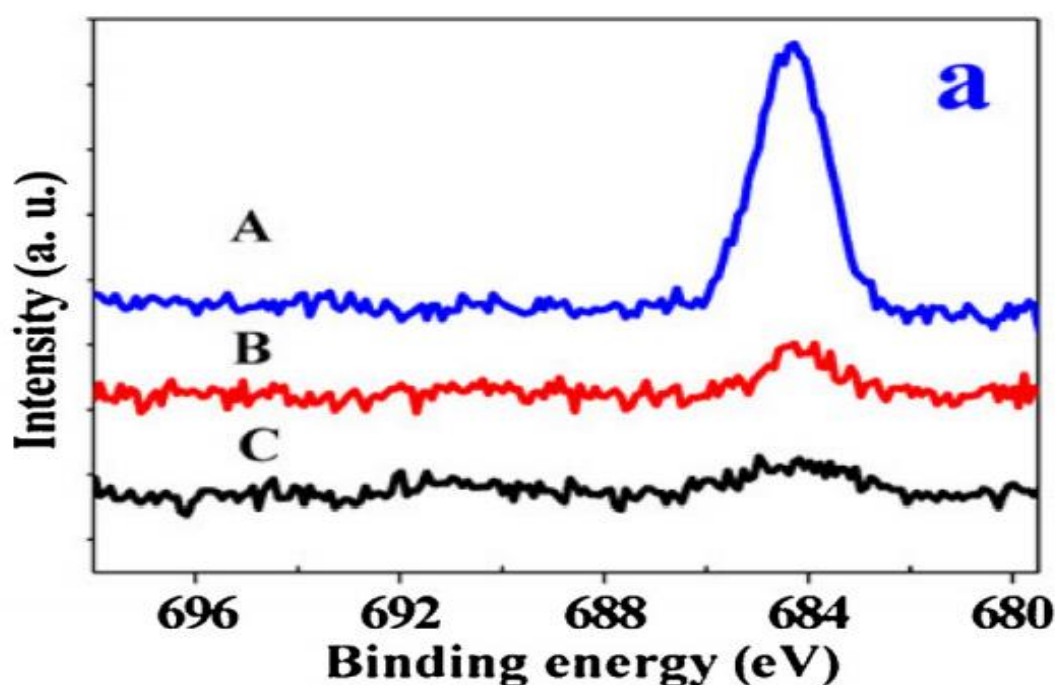

Figure 5: X-ray photoelectron spectra (XPS) for F 1s.

Observation (Figure 5):

- One peak is observed at 684.4 eV (typical value for physically absorbed F^- on the surface of TiO2 (Ti–F).
- No signal for F^- in the lattice of TiO_2 (binding energy = 688.5 eV) found.
- After NaOH wash of sample A, the F 1s signal of the B sample decreased significantly, implying that the most of F^- got removed from the TiO2 surface.
- The lowest F concentration is observed in case of sample C (exhibits the best catalytic activity).

This result indicates that presence of F^- results in the poisoning/deactivation of Pt/TiO2-NS catalysts.

Observation (Figure 6):

- Two peaks at 70.5 eV and 74.3 eV are observed, which are assigned to Pt 4f7/2 and Pt 4f5/2 of metallic Pt, respectively. Pt 4f7/2 has binding energy for Pt^0 at around 71.2 eV.
- A negative shift for Pt 4f7/2 is observed as compared to the binding energy of Pt 4f7/2 for bulk metallic Pt^0 (71.2 eV) indicating electron transfer from TiO_2 to Pt due to strong metal-support interactions (SMSI).
- Pt 4f7/2 peak of sample A exhibit positive shift as compared to samples B and C.
- Pt 4f5/2 of sample A shows one extra peak at 76.8 eV, which can be due to the adsorption of F^- on the surface of Pt NPs and the formation of Pt–F bond, leading to the transfer of electrons from Pt to highly electronegative F.
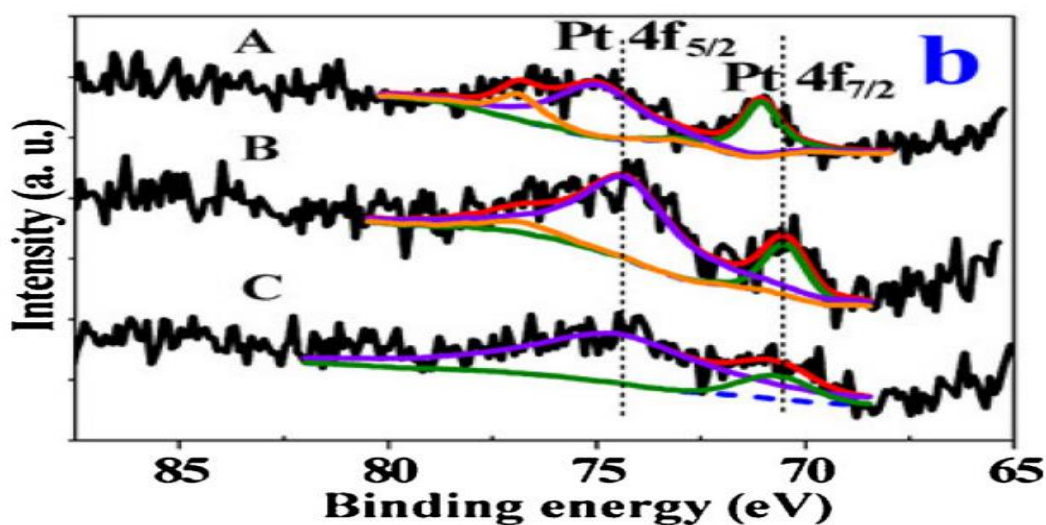

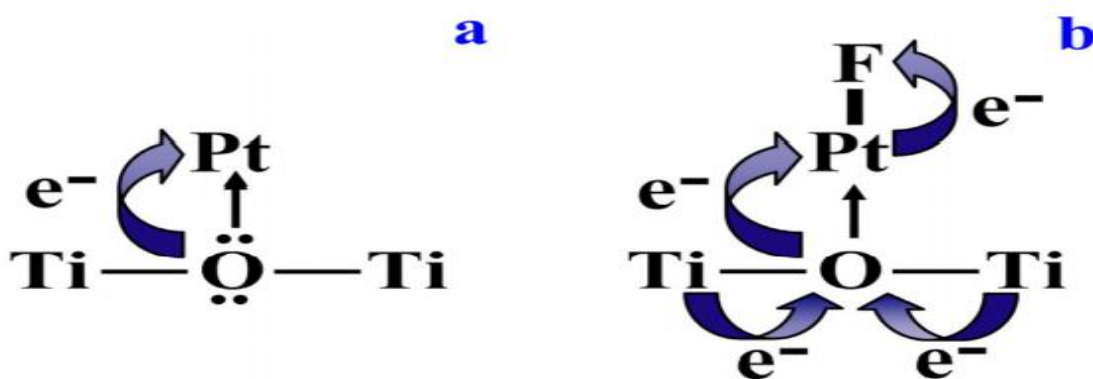*Figure 6: X-ray photoelectron spectra (XPS) for Pt 4f.*

Figure 7: (a) Schematic diagram of electron transfer between Pt and TiO2 for samples B and C; (b) electron transfer between F, Pt, O and Ti elements present in sample A.
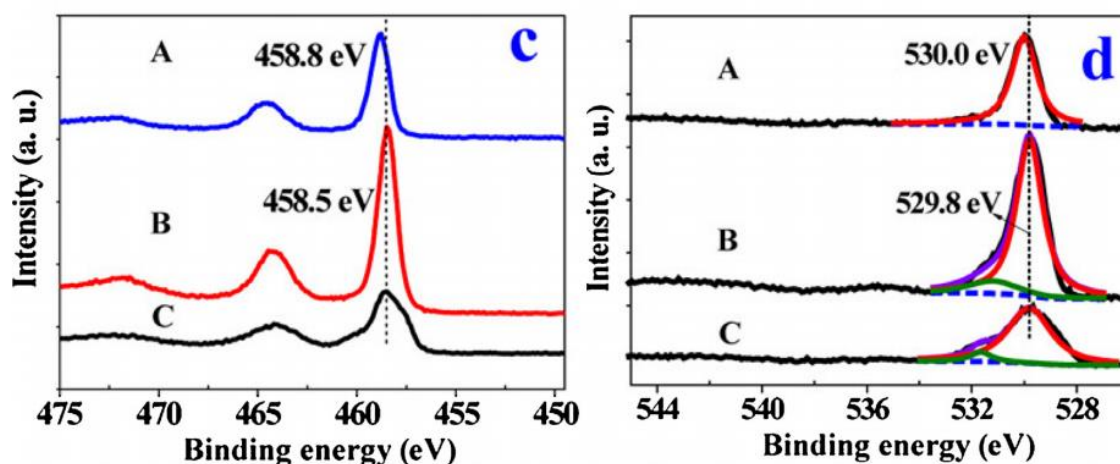
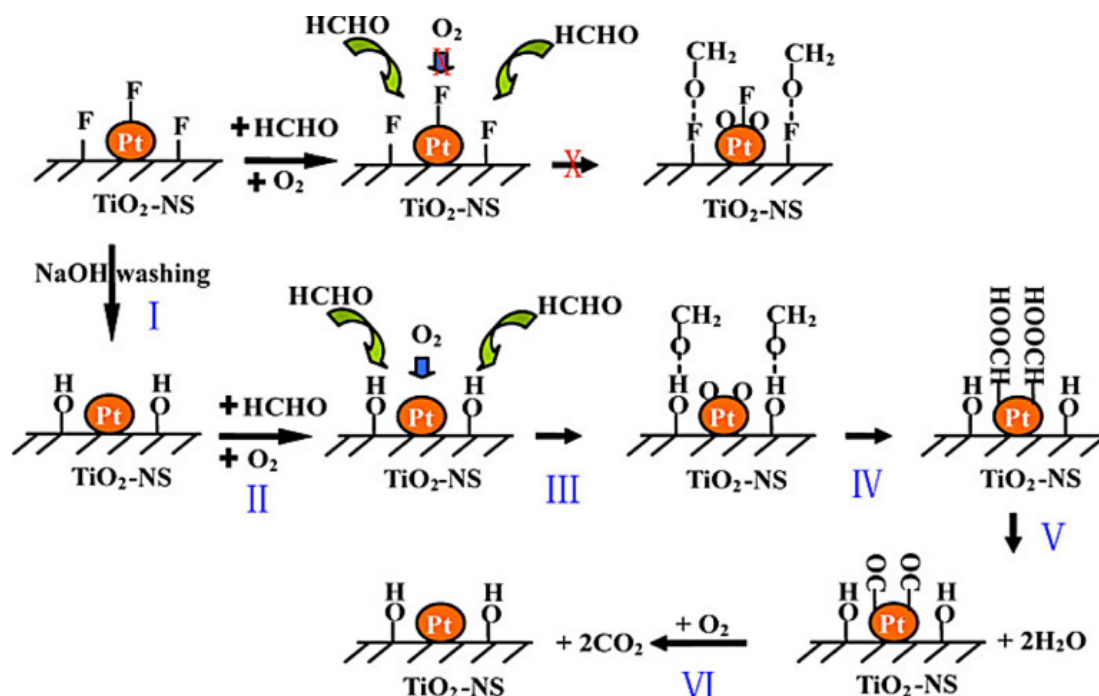*Figure 8: X-ray photoelectron spectra (XPS) for Ti 2p (c) and O 1s (d).*

Figure 9: Proposed F-poisoning/deactivation mechanism and regeneration by NaOH washing for the oxidative decomposition of HCHO on Pt/TiO2-NS.

Deactivation mechanism and regeneration analysis:

The room temperature catalytic oxidative decomposition of HCHO on Pt/TiO_2 takes place because HCHO and O_2 are first adsorbed onto TiO_2 and Pt surface. Next, O_2 becomes an active oxygen, an important stage in oxidation of HCHO. HCHO is oxidized into formate species on the surface and these species are decomposed into adsorbed CO species and H_2O, CO species react with O_2 to generate gaseous CO_2. Because of strong interactions between Pt and F on the surface of sample A, the formation of active oxygen species is difficult due to blockage of sites.

Thus, HCHO oxidation is inhibited. In order to eliminate the effect of F-poisoning, the catalyst is washed by NaOH solution in a strong basic environment.

Conclusion:

Free F⁻ adsorb easily at surface of as-prepared Pt NPs, resulting in the formation of Pt–F bond, and F-poisoning and deactivation of Pt NPs. XPS results suggest that the interaction between F and Pt is stronger than the interaction between F and Ti in basic solution. A positive shift in the binding energies of Ti 2p and O 1s is observed for the sample A sample because F induces a consecutive electron transfer, first from Pt to F, then from O to Pt and finally from Ti to O. The F-poisoned/deactivated Pt/TiO2-NS catalysts can be effectively regenerated by NaOH washing, which removes the most of F⁻ and recovers the catalytic activity of Pt/TiO2-NS.

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