

# Study on the Reaction Mechanism for Soot Oxidation Over $\text{TiO}_2$ or $\text{ZrO}_2$ -supported Vanadium Oxide Catalysts by Means of In-situ UV-Raman

Jian Liu · Zhen Zhao · Peng Liang · Chunming Xu ·  
Aijun Duan · Guiyuan Jiang · Wenyong Lin ·  
Israel E. Wachs

Received: 30 August 2007 / Accepted: 3 September 2007 / Published online: 19 September 2007  
© Springer Science+Business Media, LLC 2007

**Abstract** The reaction mechanisms for diesel soot oxidation over  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  oxide catalysts were studied by the means of in-situ UV-Raman spectroscopy. The results indicate that the formation of surface oxygen complexes (SOC) is a key step and the SOC species mainly exist as carboxyl groups. The presence of NO in the reaction gas stream can promote the formation of SOC species. For soot oxidation over  $\text{V}_4/\text{TiO}_2$  catalyst,  $\text{NO}_2$  can be produced and remarkably accelerate soot oxidation. Based on the UV-Raman experimental results, two different reaction mechanisms are proposed for soot oxidation over  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  samples, respectively.

**Keywords** Supported vanadium oxide · Catalyst · UV-Raman · In-situ · Soot · Reaction mechanism

## 1 Introduction

Soot particulate (PM) emitted from diesel engines is a serious contamination in urban areas. The combination of traps and oxidation catalysts appears to be one of the most efficient after-treatment techniques. The role of the catalyst

here is to reduce soot ignition temperature and enhance the oxidation rate of the soot collected on the filter during trap regeneration [1]. A great deal of attention has been given in the last 20 years to the research of soot catalytic combustion. Recently, some researches reported that vanadium-based catalysts were one of the most promising systems for the oxidation of diesel soot [1–3]. However, several problems are still unsolved, although the amount of work towards a better understanding is impressive. In particular, the reaction mechanism of the catalytic oxidation of soot remains unclear. It is due to the deep black colour of soot, which causes that it is very difficult in acquiring some useful information about the catalytic oxidation of soot under real reaction conditions. Some researchers investigated the catalytic oxidation of carbonaceous materials by means of in-situ IR spectroscopy using KBr as diluent [4, 5]. While the interactions between soot, metal oxides, and KBr cannot be excluded, especially when analysis is performed at high temperature. In this paper, the in-situ UV-Raman was first employed to investigate the mechanism of soot oxidation over supported vanadia catalysts. It was verified that the formation of SOC, which mainly existed as carboxyl groups, was the main reaction process during the soot oxidation over  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  catalyst.

On the other hand, Oi-Uchisawa et al. [6, 7] reported that Pt catalysts exhibited a high level of catalytic activity to promote soot oxidation in recent years. Platinum is supposed to oxidize NO to  $\text{NO}_2$ , which subsequently oxidizes soot to CO and  $\text{CO}_2$ . Therefore,  $\text{NO}_2$  is used as an intermediate to facilitate an indirect contact between the platinum catalyst and soot. The high oxidation rate of soot is due to the strong oxidizing ability of  $\text{NO}_2$ . This catalyst system is the best one so far reported for soot oxidation under loose contact conditions. However, Pt is very

J. Liu · Z. Zhao (✉) · C. Xu · A. Duan · G. Jiang  
State Key Laboratory of Heavy Oil Processing, China University  
of Petroleum, Beijing 102249, China  
e-mail: zhenzhao@cup.edu.cn

P. Liang  
Material Science & Chemical Engineering School, Eastern  
Liaoning University, Dandong, Liaoning 118003, China

W. Lin · I. E. Wachs  
In-situ Molecular Characterization and Catalysis Laboratory,  
Department of Chemical Engineering, Lehigh University,  
Bethlehem, PA 18015, USA

expensive. Thus, it will be an optimal method if  $\text{NO}_2$  can be produced and catalyze soot oxidation on the non-noble metal catalysts. In the present study a similar mechanism, i.e., the direct evidence for  $\text{NO}_2$  indirectly catalytic function is found by the means of UV-Raman spectroscopic detection on the  $\text{V}_4/\text{TiO}_2$  catalyst. Due to its strong oxidizing ability, the soot oxidation can be remarkably accelerated by  $\text{NO}_2$ . Therefore,  $\text{V}_4/\text{TiO}_2$  catalyst has higher activity than  $\text{V}_4/\text{ZrO}_2$  catalyst for soot oxidation.

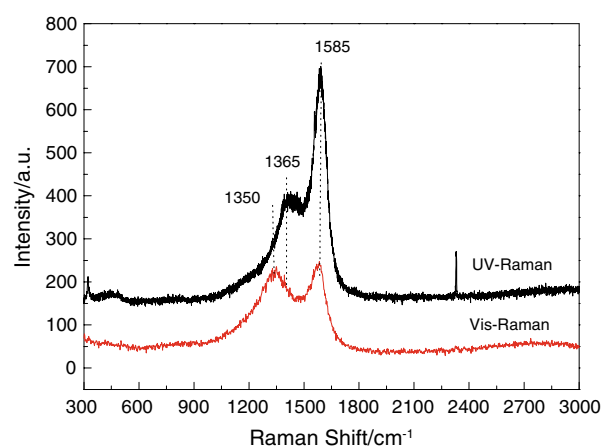
## 2 Experimental

Printex-U, which was supplied by Degussa, was used as model soot. The two samples of supported vanadia catalysts were named as  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$ , respectively, where the subscript 4 stands for the number of V atoms per 100 support metal ions. The preparation and activity measurement methods of the catalysts were described in detail in our previous work [1].

Vis-Raman spectra were performed on LabRam HR spectrometer manufactured by Horiba Jobin Yvon Company, France. The laser excitation wavelength was 514 nm. UV-Raman spectra were collected at a Jobin Yvon LabRam-HR equipped with a confocal microscope, 2,400/900 grooves/mm gratings and a notch filter. The laser excitation at 325 nm was generated from a He–Cd laser. The spectrometer resolution was less than  $2\text{ cm}^{-1}$ . The in-situ UV-Raman studies of soot oxidation over supported vanadia catalysts were loaded in powder form into an in-situ cell (Linkam, TS1500). The quartz cell is capable of operating up to  $650\text{ }^\circ\text{C}$ . The catalyst and soot (10:1, w/w) were carefully mixed in an agate mortar in order to reproduce the tight contact mode. The in-situ UV-Raman spectra were collected at different temperatures after being dehydrated at  $400\text{ }^\circ\text{C}$  for 1 h in the flowing  $\text{O}_2/\text{He}$  to desorb the adsorbed moisture. During in-situ UV-Raman testing the reactant gas stream was passed through a mixture of the catalyst and soot at a flow rate of 50 mL/min using different gas compositions: (1) 5%  $\text{O}_2$  and 0.2%  $\text{NO}$  balanced with He, or (2) 10%  $\text{O}_2$  balanced with He.

## 3 Results and Discussion

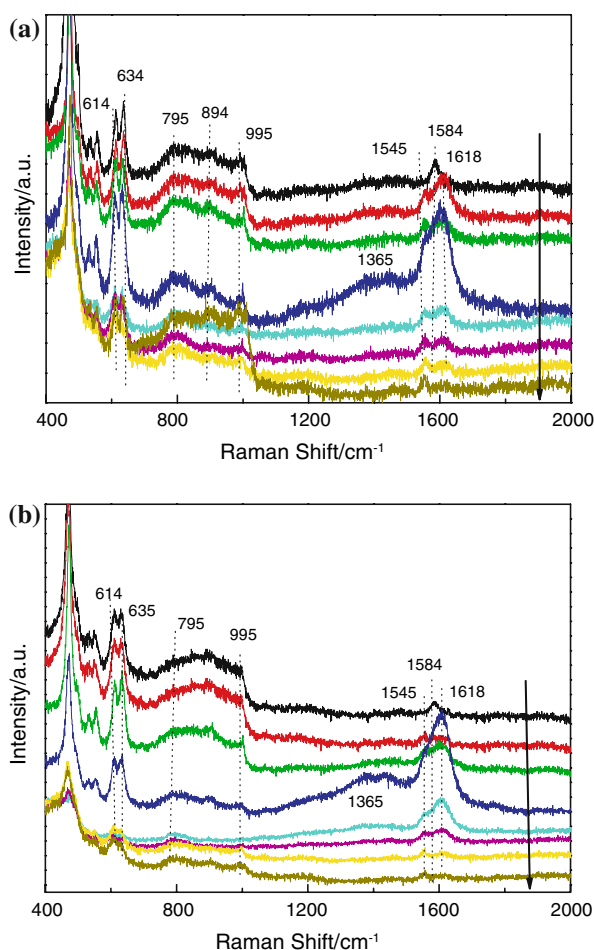
Figure 1 shows the typical UV-Raman and Vis-Raman spectra of Printex U. For UV-Raman spectrum, a strong sharp peak appears at  $1,585\text{ cm}^{-1}$  and a shoulder peak exists at  $1,365\text{ cm}^{-1}$ . For Vis-Raman spectrum, two sharp peaks appear at  $1,585$  and  $1,350\text{ cm}^{-1}$ , and their vibration intensities are basically same. According to the literature [8], the spectrum of soot generally exhibit two broad and strong overlapping peaks with intensity maxima at



**Fig. 1** The UV-Raman and Vis-Raman spectra of Printex U

$\sim 1,580\text{ cm}^{-1}$  and at  $\sim 1,350\text{ cm}^{-1}$ . The band at around  $1,580\text{ cm}^{-1}$  is corresponding to an ideal graphitic lattice vibration mode with  $\text{E}_{2g}$  symmetry, and the band at  $1,350\text{--}1,365\text{ cm}^{-1}$  is assigned to a disorder graphitic lattice vibration mode with  $\text{A}_{1g}$  symmetry [8]. Compared to the Vis-Raman spectrum, the higher vibration intensity of the peak at  $1,585\text{ cm}^{-1}$  in the UV-Raman spectrum indicates that UV-Raman is more sensitive to the  $\text{E}_{2g}$  symmetry vibration.

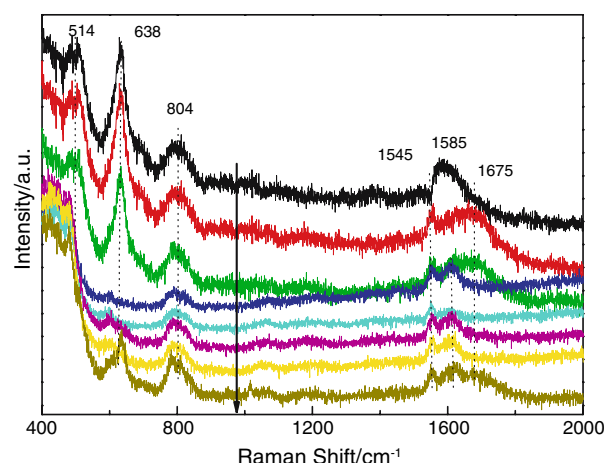
The investigation of the reaction mechanism of soot oxidation was carried out on  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  catalysts. Figure 2 shows the in-situ UV-Raman spectra of  $\text{V}_4/\text{ZrO}_2$  catalyst for soot oxidation at different temperatures. At  $(\text{NO}+\text{O}_2)/\text{He}$  atmosphere, as shown in Fig. 2a, the peaks below  $1,200\text{ cm}^{-1}$  are due to the vanadyl or zirconium oxides. The peak at  $1,584\text{ cm}^{-1}$  is corresponding to an ideal graphitic lattice vibration mode with  $\text{E}_{2g}$  symmetry and at  $1,365\text{ cm}^{-1}$  is assigned to the  $\text{A}_{1g}$  symmetry vibration of the disorder graphitic lattice. When reaction temperature exceeds  $100\text{ }^\circ\text{C}$ , two new peaks at  $1,545$  and  $1,618\text{ cm}^{-1}$  appear in the UV-Raman spectra. According to the literature, the band at  $1,545\text{ cm}^{-1}$  is ascribed to the ring stretching vibrations of aromatic moieties, and the band at  $1,618\text{ cm}^{-1}$  may be assigned to the  $\nu_A$  vibration of  $\text{COO}^-$  and benzene ring stretching. It indicates that the SOC species mainly exist as carboxyl groups [9]. With the increase of the reaction temperature, the intensities of the peaks gradually increase, indicating that the vibration enhances. When reaction temperature exceeds  $300\text{ }^\circ\text{C}$ , the intensities of the both peaks gradually decrease and they disappear at last. It may be due to the reaction has completed and soot has been completely oxidized. For soot oxidation over  $\text{V}_4/\text{ZrO}_2$  catalyst at  $\text{O}_2/\text{He}$  atmosphere, as shown in Fig. 2b, the positions of the absorption peaks are basically unchanged compared with the UV-Raman spectra in Fig. 2a. It indicates that the peaks at  $1,545$  and



**Fig. 2** The in-situ UV-Raman spectra of  $V_4/ZrO_2$  catalyst during soot oxidation at different temperatures (lowest temperatures on top: ambient, 100, 200, 300, 400, 500, 600, and 650 °C). Reactant gas compositions: (a) 5%  $O_2$  and 0.2% NO balanced with He and (b) 10%  $O_2$  balanced with He

$1,618\text{ cm}^{-1}$  cannot be attributed to the stretching vibration of the species containing nitrogen. Figure 2a shows that the peaks at  $1,545$  and  $1,618\text{ cm}^{-1}$  appear in the UV-Raman spectra of  $V_4/ZrO_2$  catalyst for soot oxidation at  $100\text{ }^\circ\text{C}$ . However, Fig. 2b shows that they do not appear until the reaction temperature reaches  $200\text{ }^\circ\text{C}$ . It indicates that the formation of SOC is easier in  $(NO + O_2)/He$  atmosphere than in  $O_2/He$  atmosphere.

Figure 3 shows the in-situ UV-Raman spectra of  $V_4/TiO_2$  catalyst for soot oxidation at different temperatures. The reactant gases contains 5%  $O_2$ , 0.2% NO and diluted gas He. The peaks below  $1,200\text{ cm}^{-1}$  are due to the vibration of vanadyl species or anatase. The peak at  $1,585\text{ cm}^{-1}$  is assigned to the  $E_{2g}$  symmetry of soot. Several new vibration peaks at  $1,545$ ,  $1,618$  and  $1,675\text{ cm}^{-1}$  appear in the UV-Raman spectra. The foregoing two peaks may be attributed to the vibration of carboxyl groups [9], and the last one may be due to the  $\nu_{as}$  vibration of  $NO_2$  [10, 11].



**Fig. 3** The in-situ UV-Raman spectra of  $V_4/TiO_2$  catalyst during soot oxidation at different temperatures (lowest temperatures on top: ambient, 100, 200, 300, 400, 500, 600, and 650 °C). Reactant gas compositions: 5%  $O_2$  and 0.2% NO balanced with He

With the increase of the reaction temperature, the intensity of the peak at  $1,675\text{ cm}^{-1}$  gradually decreases, and when the reaction temperature increases to  $300\text{ }^\circ\text{C}$ , the peak disappears. This phenomenon indicates that  $NO_2$  has decomposed due to the thermodynamic unstability of  $NO_2$  at high temperature. However, a small amount of  $NO_2$  is over again produced at  $650\text{ }^\circ\text{C}$ . It is ascribed to the complete oxidation of soot disturbing the chemical equilibrium of NO and  $NO_2$ . Thus, a very weak peak at  $1,675\text{ cm}^{-1}$  appears again the UV-Raman spectra of  $V_4/TiO_2$  catalyst.

The study on the mechanism for catalytic oxidation reactions of carbonaceous materials has been the subject of some researches over the last decades [12, 13]. In the previous studies, usually KBr was used as a diluent in IR spectroscopic studies to obtain high quality in-situ spectra of carbonaceous materials. However, interactions between SOC and/or metal oxides and KBr could not be excluded, especially when analyses were performed at elevated temperatures. While carbon black significantly absorbed IR radiation over the entire region from  $400$  to  $4,000\text{ cm}^{-1}$ , therefore, it was limited to characterize the soot oxidation over metal oxides by using in-situ IR method. The Ultra-violet Raman spectroscopy is a powerful tool for the study of solid catalysts [14, 15]. UV-Raman can effectively monitor the reaction of soot oxidation over transition metal oxide catalysts. It does not need to dilute with KBr. In this study in-situ UV-Raman spectroscopy for the soot oxidation reaction was performed at various temperatures on the  $V_4/ZrO_2$  and  $V_4/TiO_2$  catalysts. Raman spectra taken during the oxidation of soot clearly show that the surface oxygen species can undergo significant structural changes depending on the oxidation temperature and the composition of the support. On  $V_4/TiO_2$ , the vibration band centered around  $1,675\text{ cm}^{-1}$  may be assigned to the  $\nu_{as}$

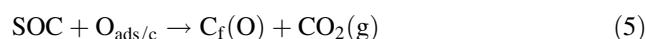
vibration of  $\text{NO}_2$  [10, 11]. Attributing to its thermodynamic unstability,  $\text{NO}_2$  will decompose with the increase of the reaction temperature. The in-situ UV-Raman spectra of  $\text{V}_4/\text{TiO}_2$  exhibit that the intensity of the peak at  $1,675\text{ cm}^{-1}$  gradually decreases and the peak disappears when the reaction temperature increases to  $300\text{ }^\circ\text{C}$ . On  $\text{V}_4/\text{TiO}_2$  and  $\text{V}_4/\text{ZrO}_2$ , the peaks at  $1,554$  and  $1,608\text{ cm}^{-1}$  indicate the formation of SOC on Printex-U in the presence of catalyst. It is different from the literature report that the SOC species mainly exist as quinone, lactones and ether-like complexes, and they are mainly present as carboxyl groups identified with in-situ UV-Raman spectroscopy in this work [13, 16]. Compared Fig. 2a with Fig. 3, it can be found that SOC appears on  $\text{V}_4/\text{ZrO}_2$  at  $100\text{ }^\circ\text{C}$ , while it forms on  $\text{V}_4/\text{TiO}_2$  at ambient temperature. It indicates that SOC is more easily produced on  $\text{V}_4/\text{TiO}_2$  than  $\text{V}_4/\text{ZrO}_2$ . Similarly, compared Fig. 2a with b, it can also be found that SOC appears under the  $(\text{NO} + \text{O}_2)/\text{He}$  atmosphere at  $100\text{ }^\circ\text{C}$ , while it forms under the  $\text{O}_2/\text{He}$  atmosphere until the reaction temperature reaches  $200\text{ }^\circ\text{C}$  on  $\text{V}_4/\text{ZrO}_2$  samples. It can be concluded that SOC is more easily produced under the  $(\text{NO} + \text{O}_2)/\text{He}$  atmosphere than under the  $\text{O}_2/\text{He}$  atmosphere. The results indicate that the presence of NO in reaction gas stream can promote the production of SOC species. Combined with the results of the catalytic activities in Table 1, it can be concluded that the formation of SOC species not only lower the peak temperatures of soot oxidation ( $T_m$ ), but also it increases the selectivity to  $\text{CO}_2$  formation ( $S_{\text{CO}_2}$ ). In a word, the results of in-situ UV-Raman and the catalytic activity measurements demonstrate the formation of SOC is a fundamental process taking place in the catalytic soot oxidation over  $\text{V}_4/\text{ZrO}_2$  and  $\text{V}_4/\text{TiO}_2$  samples.

On the other hand, some reports have demonstrated that  $\text{NO}_2$  is much more reactive towards soot oxidation than NO or  $\text{O}_2$ . Oi-Uchisawa et al. [6, 7] reported that a platinum catalyst could oxidize NO to  $\text{NO}_2$ , which subsequently oxidize soot to CO and  $\text{CO}_2$ . Thus,  $\text{NO}_2$  is used as an intermediate to facilitate an indirect contact between the platinum catalyst and soot. This mechanism subtly changed solid (soot)–solid (catalyst) contact into solid (soot)–gas ( $\text{NO}_2$ )–solid (catalyst) contact. Thus, the platinum catalyst system obtained the best results so far reported for soot oxidation under loose contact conditions. The high oxidation rate of soot is due to the strong oxidizing ability of

$\text{NO}_2$ . A similar mechanism is found for soot oxidation over the  $\text{V}_4/\text{TiO}_2$  catalyst in this study. As shown in Fig. 3, the direct evidence of  $\text{NO}_2$  formation over the  $\text{V}_4/\text{TiO}_2$  sample is first found by means of UV-Raman spectroscopic measurement. Due to the strong oxidation capacity of  $\text{NO}_2$ , the soot oxidation can be remarkably accelerated by  $\text{NO}_2$ . Therefore,  $\text{V}_4/\text{TiO}_2$  catalyst has higher activity than  $\text{V}_4/\text{ZrO}_2$  catalyst. This conclusion is verified by the results of the catalytic activities in Table 1. If NO is not contained in the reactant gases, the discrepancy of  $T_m$  is only  $5\text{ }^\circ\text{C}$  and  $S_{\text{CO}_2}^m$  is almost same for soot oxidation over  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  catalysts. Whereas, when NO is present in the reactant gas stream, compared to soot oxidation over  $\text{V}_4/\text{ZrO}_2$  catalyst,  $T_m$  decreases by  $44\text{ }^\circ\text{C}$  and  $S_{\text{CO}_2}^m$  increases by 2% point for that over  $\text{V}_4/\text{TiO}_2$  catalyst.

The combination of fundamental molecular structural information and in-situ UV-Raman spectra has resulted in a molecular-level understanding of structure–activity relationships for soot oxidation reaction. Taking into account the above experimental results and discussion, two different reaction mechanisms can be proposed for soot oxidation over  $\text{V}_m/\text{ZrO}_2$  or  $\text{V}_m/\text{TiO}_2$  samples.

#### Mechanism 1:



where,  $\text{M}_x\text{O}_y$  refers to  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  catalysts, and  $\text{C}_f$  refers to reactive free carbon, and  $\text{C}_f(\text{O})$  refers to the unreactive surface oxygen complexes, and SOC stands for the reactive surface oxygen complexes. According to our previous results [1, 17–19], the catalytic active sites of supported vanadia catalysts for soot oxidation reaction are mainly polymeric vanadyl V–O–V species, while crystalline bulk  $\text{V}_2\text{O}_5$  and isolated vanadium oxide are supposed

**Table 1** The peak temperature ( $T_m$ ) and the selectivity to  $\text{CO}_2$  formation at  $T_m$  temperature  $S_{\text{CO}_2}^m$  for soot oxidation over  $\text{V}_4/\text{ZrO}_2$  or  $\text{V}_4/\text{TiO}_2$  catalysts at different reactant gas compositions

Catalysts	$\text{V}_4/\text{ZrO}_2$	$\text{V}_4/\text{ZrO}_2$	$\text{V}_4/\text{TiO}_2$	$\text{V}_4/\text{TiO}_2$
Reactant gas compositions	5% $\text{O}_2$ + 0.2% NO + He	10% $\text{O}_2$ + He	5% $\text{O}_2$ + 0.2% NO + He	10% $\text{O}_2$ + He
$T_m$ ( $^\circ\text{C}$ )	433	435	389	430
$S_{\text{CO}_2}^m$ (%)	89	87	90	87

to be less active than polymeric surface vanadyl species.  $V_4/ZrO_2$  or  $V_4/TiO_2$  catalysts have high concentration of polymeric vanadyl species. Thus, the active sites of  $M_xO_y$  should be V–O–V species supported on  $ZrO_2$  or  $TiO_2$  supports. Moreover, the difference between  $O_2$  and  $O_{ads}$  should be explicitly noticed.  $O_2$  denotes a much more free state of oxygen, being mobile by surface migration on the edges or basal plane of the carbonaceous material, and  $O_{ads}$  stands for the adsorption oxygen on the surface of catalyst. In the above notation,  $C_f(O)$  and SOC refer to surface oxygen complexes in which the chemical interaction between the carbon and oxygen atom is so strong that the oxygen atom can be considered to be chemically bonded. In the literature [13, 16], these surface oxygen complexes may be composed of carbonyl and ether groups as lactone, quinine, and acid anhydride functional groups. However, SOC are typically composed of carboxyl in this work. This mechanism is consistent with the reference [16].

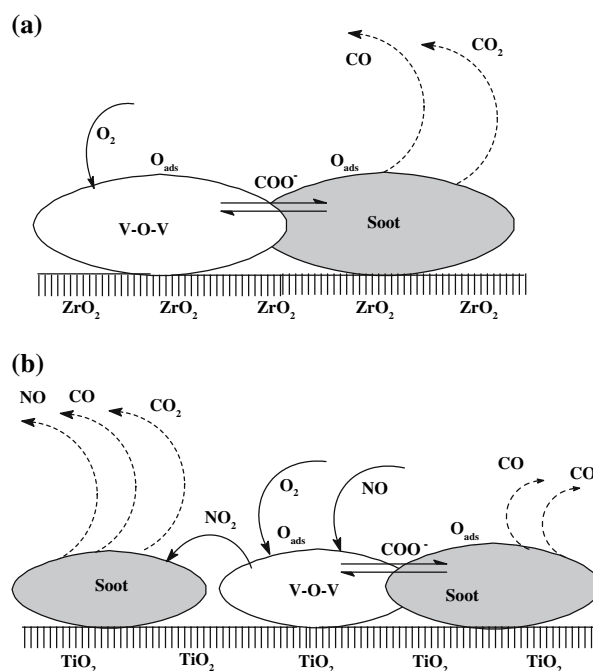
Gaseous oxygen is adsorbed dissociatively on the catalyst surface (reaction 1) and then the oxygen atoms adsorbed on soot ( $O_{ads/C}$ ) are formed by the transferring of  $O_{ads}$  to the surface of soot (reaction 2). The resulting species attack the reactive free carbon to give the unreactive surface oxygen complex intermediate  $C_f(O)$  (reaction 3). They react with  $O_{ads/C}$  to produce reactive surface oxygen complex intermediate SOC (reaction 4). These complexes exist as carboxyl groups ( $COO^-$ ).  $O_{ads/C}$  is added to such complexes through reaction, and upon desorption of a CO and a  $CO_2$  gaseous product molecules an adjacent carbon atom forms a new complex (reactions 5 and 6). Surface oxygen complexes increase the rates of catalytic oxidation of Printex U.  $CO_2/CO$  ratios also increase in the presence of surface oxygen complexes.

For soot oxidation over  $V_4/ZrO_2$  catalyst, only SOC intermediate species are detected and the reaction mainly follows the mechanism 1. Thus, the whole reaction mechanism can be described in the Fig. 4a. For soot oxidation over  $V_4/TiO_2$  catalyst,  $NO_2$  is also detected besides SOC. Therefore, the following reaction process must be considered besides the mechanism 1 shown above.

Mechanism 2:



Thus, both the formation of SOC and the production of  $NO_2$  play important roles in soot oxidation over  $V_4/TiO_2$  catalyst. In other words, two reaction pathways to oxidize soot take place simultaneously over  $V_4/TiO_2$  catalyst. The whole reaction process can be described in the Fig. 4b.



**Fig. 4** The schemes of the reaction mechanisms for soot oxidation over  $V_4/ZrO_2$  or  $V_4/TiO_2$  catalysts: (a)  $V_4/ZrO_2$  and (b)  $V_4/TiO_2$

## 4 Conclusions

The formation of carboxyl group species in the catalytic oxidation of soot over  $V_4/ZrO_2$  and  $V_4/TiO_2$  catalysts was observed by in-situ UV-Raman spectroscopy. The presence of  $NO$  in the reaction gas stream can promote the formation of SOC species. Based on the in-situ UV-Raman experimental results, two different reaction mechanisms to oxidize soot over  $V_4/ZrO_2$  or  $V_4/TiO_2$  samples are proposed. For soot oxidation over  $V_4/ZrO_2$  catalyst, only SOC intermediate species are detected and the reaction mainly follows the mechanism of the formation of SOC. For soot oxidation over  $V_4/TiO_2$  catalyst,  $NO_2$  is also detected besides SOC. The reaction simultaneously follows both the mechanism of the formation of SOC and the mechanism of the indirect catalysis of  $NO_2$ .

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (Nos. 20473053 and 20525021), the Beijing Natural Science Foundation (No. 2062020), the 863 Program of China (No. 2006AA06Z346), and the Scientific Research Key Foundation for the Returned Overseas Chinese Scholars of State Education Ministry.

## References

- Liu J, Zhao Z, Xu C, Duan A, Zhu L, Wang X (2005) Appl Catal B 61:36
- Zhao Z, Liu J, Xu C, Duan A, Kobayashi T, Wachs IE (2006) Top Catal 38:309



3. Setiabudi A, Allaart NK, Makkee M, Moulijn JA (2005) *Appl Catal B* 60:233
4. Mul G, Neeft JPA, Kapteijn F, Moulijn JA (1998) *Carbon* 36: 1269
5. Minogue N, Riordan E, Sodeau JR (2003) *J Phys Chem A* 107: 4436
6. Oi-Uchisawa J, Obuchi A, Wang SD, Nanba T, Ohi A (2003) *Appl Catal B* 43:117
7. Oi-Uchisawa J, Wang SD, Nanba T, Ohi A, Obuchi A (2003) *Appl Catal B* 44:207
8. Sadezky A, Muckenhuber H, Grothe H, Niessner R, Poschl U (2005) *Carbon* 43:1731
9. Alvarez-Puebla RA, Garrido JJ, Aroca RF (2004) *Anal Chem* 76:7118
10. Amariei D, Coutheux L, Rossigno S, Kappenstein C (2007) *Chem Eng Process* 46:165
11. Minogue N, Riordan E, Sodeau JR (2003) *J Phys Chem A* 107:4436
12. Kim UJ, Furtado CA, Liu X, Chen G, Eklund PC (2005) *J Am Chem Soc* 127:15437
13. Mul G, Kapteijn F, Moulijn JA (1997) *Appl Catal B* 12:33
14. Zhang J, Li M, Feng Z, Chen J, Li C (2006) *J Phys Chem B* 110:927
15. Li C (2003) *J Catal* 216:203
16. Stanmore BR, Brilhac JF, Gilot P (2001) *Carbon* 39:2247
17. Liu J, Zhao Z, Xu C, Duan A, Zhu L, Wang X (2006) *Catal Today* 118:315
18. Liu J, Zhao Z, Xu C (2005) *Acta Phys-Chim Sin* 21:156
19. Liu J, Zhao Z, Xu C (2005) *Chem J Chinese U* 26:1290