Atomic Layer Deposition of TiO₂ Thin Films on the Inner Walls of Steel Tubes Increases Anti-coking Properties

Changfa Zhu, Fei Ma, Zhengfei Dai, and Dayan Ma*

ABSTRACT: To suppress catalytic coking, TiO₂ passivation films were deposited on the inner walls of SS316 stainless steel tubes by atomic layer deposition (ALD). Indentation test results showed a platform on the indentation curve of TiO₂ films grown over 2000 ALD cycles due to internal stress-induced microcracks. In coking experiments, the TiO₂-coated tubes exhibited a higher heat flux and lower pressure difference than bare ones. Analysis of the coking surface revealed that TiO₂ thin film passivation can reduce the size and number of particulate deposits. At the same time, passivation treatment inhibits the formation of filamentous carbon and improves anti-coking performance by reducing the ability of the tube to adsorb amorphous deposition products. The coking surfaces of TiO₂-coated tubes had less graphitization, indicating that the coking products had fewer defects and lower activated carbon contents.

1. INTRODUCTION

Poor thermal management is one of the important factors that limit hypersonic flight. In recent decades, endothermic hydrocarbon fuel has become a major prospect in the evolution of advanced aircraft.¹⁻³ Large-molecule hydrocarbon fuels absorb a large amount of heat and undergo a cracking reaction to form carbon deposits in a process called coking. Coking increases heat transfer resistance and leads to a pressure drop in cooling channels. Flow paths can even become blocked, with disastrous consequences. Generally, there are three mechanisms of carbon formation: catalytic coking,⁴ radical coking,⁵,⁶ and droplet condensation coking.⁷ Catalytic coking involving metal particles is the dominant form occurring at high temperatures. Fe and Ni in tubes commonly catalyze coking reactions.⁸ Coating the inner walls of these tubes has proven to be an effective anti-coking method.⁹

Chemical vapor deposition (CVD) and the sol–gel method are effective approaches to producing SiO₂, Al₂O₃, TiO₂, and TiN passivation films that can be used to coat tubes subject to coking.¹⁰⁻¹² However, the high deposition temperature of CVD changes the original crystal structure of the substrate.¹³ Sol–gel inevitably produces microcracks during the sintering process, and microcracks in sol–gel coatings limit their anti-coking performance.¹⁴ Atomic layer deposition (ALD) can be used to grow continuous, uniform, thin films at the atomic scale.¹⁵ Additionally, the temperature required for ALD deposition is lower than that needed for CVD and sol–gel, which can avoid damage to the substrate. In recent years, ALD has been widely explored for preparing metals and metal oxide thin films. Hui et al. studied the influence of ALD passivation treatment on coking morphology.¹⁶ TiO₂ films are useful as protective coatings due to their good chemical stability and thermal shock resistance.¹⁷,¹⁸ In this paper, TiO₂ passivation films were prepared on an SS316 substrate. Indentation tests were conducted to investigate the mechanical properties of the TiO₂ coatings. The anti-coking
performance of the TiO₂ coatings was studied via electrically heated tube tests. The endothermic 851-2 aviation kerosene fuel was used as a coolant, its main components being methylcyclohexane and chain alkanes. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy were used to characterize the microstructure of the TiO₂ coatings and coking deposition.

2. RESULTS AND DISCUSSION

2.1. Characterization of TiO₂ Passivation Films. Figure 1 shows the XRD patterns of the thin films, in which only peaks of anatase TiO₂ can be identified (JCPDF no.83-2243). In the 500-cycle TiO₂ thin films, only a characteristic peak of anatase with a (211) crystal orientation was found. However, (101), (200), (211), and (204) peaks of anatase TiO₂ were identified at 25°, 48°, 55°, and 62°, respectively, in the 1500- and 2000-cycle TiO₂ thin films, with a preferred (101) orientation.

Kinetically, anatase TiO₂ is stable below 600 °C but will transform into a more stable crystal structure at 600–700 °C. Rutile TiO₂ exhibits greater thermal stability, hardness, and Young’s modulus than anatase and is appropriate for application as protective layers. The TiO₂ films were annealed in a vacuum at 800 °C at a heating rate of 10 °C/min with argon protection. After annealing at 800 °C, the XRD spectra of the TiO₂ film showed weak diffraction peaks of rutile phases (211) and (311) at 54° and 70°, respectively, indicating that the anatase phase began to transform into the rutile phase. Because the annealing time was short, there should have been a mixed phase of anatase and rutile at this time.

Figure 2 shows the cross-sectional images of TiO₂ thin films made with different cycles. There is a clear boundary between the TiO₂ thin film and Si wafer, and the cross-sectional morphology of the TiO₂ films is uniform and dense. The 1500-cycle TiO₂ film (Figure 2b) exhibits obvious columnar crystals with thicknesses of 118.3, 158.5, and 260.0 nm. The average TiO₂ film deposition rate was 1.1–1.3 Å/cycle, which is consistent with the deposition rates reported in the literature.

The morphologies of bare and 2000-cycle TiO₂-coated tubes are presented in Figure 3. The bare tube (Figure 3a) had many microcracks, which are harmful to high-temperature performance and corrosion resistance. However, precursors are always preferred on rough surfaces and produce large interactions with the tubes. Confocal microscopy shows that the inner surfaces of bare tubes were rough with many gaps (Figure 3c), while 2000-cycle TiO₂-coated tubes were relatively smooth (Figure 3d). In the same location, the surface roughness after passivation was 8.208 μm, which is less than a value of 14.798 μm for the bare tubes. The elemental compositions of bare and TiO₂-coated tubes are listed in Table 1. The contents of Fe (65.69%) and Ni (8.96%) on the bare tubes were as high as 71.80%. However, Ti (47.81%) and O (32.94%) were the most abundant elements on the TiO₂-coated tubes.

The mechanical properties of TiO₂ thin films can be measured by nano-indentation. The 2000-cycle TiO₂ thin-film sample showed an obvious load buffer during the loading process (Figure 4a), indicating that as the deposition time increased, internal stress accumulated and the normal force loading process may have produced crushing or microcracks. Therefore, in the investigation of coating tubes to increase their anti-coking performance, the TiO₂ film samples made with over 2000 ALD cycles were not considered in order to reduce the influence caused by internal stress.

The hardness and elastic modulus of TiO₂ thin films were calculated according to eqs 1 and 2. The hardness and elastic modulus of different samples are shown in Figure 4b. Thickness has little effect on hardness and elastic modulus. The hardness and elastic modulus were 10 and 136 GPa, respectively. These values correspond to anatase TiO₂ films of 10–14 and 130–150 Gpa, respectively.23

\[
H = \frac{P_{\text{max}}}{A}
\]
\[ E_s = \frac{1}{\beta} \sqrt{\frac{S}{A}} \]  

in which \( A \) is the contact area between the indenter and sample, \( S \) is the material stiffness, and \( \beta \) is a constant (1.034).

The 1500- and 2000-cycle TiO2 thin-film-passivated tubes were placed in a heating furnace at a constant temperature of 800 °C for 30 min and then taken out to cool in the air. The bonding strengths of the film and substrate at high temperatures were investigated, with images shown in Figure 4c,d. Some microcracks and pits are visible on the surface of the 1500-cycle TiO2 sample (Figure 4c), while the 2000-cycle sample has a higher microscopic flatness and excellent adhesion to the substrate (Figure 4d). Therefore, the anti-coking performance of the 2000-cycle TiO2 film-passivated tube was investigated.

### 2.2. Anti-coking Performance of the TiO2 Coating

Figure 5 illustrates the fluctuations in heat flux and the decrease in pressure during the 800 °C holding stages. After passivation, the heat flux density of the tube (Figure 5a) increases by 15–20 kW/m². While the bare tube was kept at 800 °C, the average system pressure drop was 45.33 kPa. However, the pressure drop of the TiO2-coated tube was 44.54 kPa. In addition, the standard deviation of the bare tube was 2.12, which is higher than that of the 2.07 of the TiO2-film-passivated tube, since the thermal conductivity of TiO2 film is 0.7–1.7 W m⁻¹ K⁻¹,₂₄ which is lower than that of the SS316 substrate. Thermal conductivity is related to the degree of coking occurring during the anti-coking experiment.

After the anti-coking test, the specimens were cut at different positions. The formula for the coking ratio \( \eta \) is calculated as follows:

\[ \eta = \frac{m_1 - m_2}{m_2} \]  

where \( m_1 \) and \( m_2 \) are the masses of the tube before and after the coking experiment, respectively.

The wall temperature and carbon deposition along the tube are shown in Figure 6. At temperatures > 600 °C, catalytic and free radical coking are the main coking mechanisms. At a fuel outlet temperature of 800 °C, the temperatures differ along the tube (Figure 6a). At 40–50 cm, the wall temperature of the bare tube is <800 °C. The temperature is 50–60 °C lower at
the same location on the TiO$_2$-coated tube. However, no obvious difference in carbon deposition is evident. The highest wall temperature exceeds 850 °C near the outlet. The deposition rate of carbon changes significantly with wall temperature (Figure 6b). At 60–100 cm along the tube, the carbon deposition ratio of the bare tube exceeds 25% and reaches a maximum of 40.49%. However, the carbon deposition ratio of the TiO$_2$-coated tube is significantly

Figure 4. Results of indentation testing of TiO$_2$ thin-film samples. (a) Nano-indentation loading and unloading curves. (b) Elastic modulus and hardness vs ALD cycles. SEM images of the morphology of (c) 1500-cycle and (d) 2000-cycle TiO$_2$-film-passivated tubes after 800 °C thermal vibration for 30 min.

Figure 5. Fluctuations with experimental time: (a) heat flux and (b) pressure drop.
lower, with a maximum of 17.61%. On the bare tube, Fe and Ni catalyze fuel cracking, which forms more carbon deposits. However, only the free radical coking reaction occurs after passivation, causing significantly reduced carbon deposits. At the same time, the upstream coking products flow along with fuel and converge in the middle and downstream positions, resulting in an increase in the carbon deposition rate at 60–100 cm along the tube.

2.3. Coking Morphology. As shown in Figure 7, the bare and TiO₂-coated tubes exhibit cobblestone surfaces after the coking experiments, as has been reported previously. However, the cobbles are significantly reduced on the TiO₂-passivated tube. As shown in Figure 7a, the cobble particles have diameters of 10–25 μm on the bare tubes and 5–12.5 μm on the TiO₂-coated tubes. Roughness and cracks affect the amount of coking precursors adsorbed on the surface. More coking precursors are absorbed on the surface of bare tubes than TiO₂-coated tubes. This is because the TiO₂ film prevents direct contact between the fuel and steel tube, which inhibits the progress of the catalytic coking reaction. The coking precursor generates carbon deposits via a dehydrogenation reaction.

Selected images of carbon deposits are shown in Figure 8. Generally, different shapes of carbon deposits were produced. Filamentous coke is produced by the catalytic mechanism. Filamentous carbon can be found on bare tube samples (Figure 8a,b), which are able to trap tar droplets before reaching the solid substrate, leading to particle magma and “cauliﬂower”-shaped particle magma (Figure 8a). Moreover, these filamentous carbons can be agglomerated with amorphous carbon or coke layers (Figure 8b), eventually clogging the entire tube and rendering it ineffective. Figure 8c,d shows the coking morphology on the TiO₂-coating tube; a continuous and smooth layer of coke can be observed (Figure 8c). Small particles are randomly distributed on the coking layers. No filamentous carbon was found on the coking surface after passivation. The cokes in the reactor are produced through the radical coking mechanism. Large amounts of free radicals form carbon deposits through a Diels−Alder-type reaction. A complete layer is formed on the coking surface. Observation at higher magnification shows that there are many holes in the carbon deposit layers (Figure 8d). This is caused by the escape of hydrogen produced in the thermal cracking reaction.

Figure 9 shows the SEM images and EDS spectra of the cokes on the bare and TiO₂-coated tubes. As shown in Figure 9a, amorphous deposits are distributed on most of the TiO₂-coated tube surface. A continuous coking layer with granular deposits is formed on the surface of the bare tube (Figure 9b). The elemental compositions of the coking surfaces on the bare
and TiO2-coated tubes are listed in Table 2. The content of elemental C is 31.86% on the bare tube, which is significantly higher than that on the TiO2-film-passivated tube (11.13%). The Fe content of 59.98% on the bare tube is higher than the 44.29% on the TiO2-coated tube. This indicates that the TiO2 film can reduce coking deposition. In the early stage of the coking reaction, the TiO2 film prevents contact between the Fe/Ni and the fuel, thereby avoiding the generation of filamentous carbon and reducing the carbon deposition ratio. However, the Fe content on the coking surface is higher than 12.65% in Figure 6b, which indicates that some Fe atoms diffused through the TiO2 film during the experiment. This explains the mechanism of failure of the TiO2 film’s anti-coking function and provides an idea of how to extend the anti-coking properties.

After ultrasonication of coking samples in alcohol for 1 h, the resulting solution was dropped on 200-mesh ultra-thin copper mesh. As shown in Figure 10a, filamentous carbon with diameters of 20–30 nm can be clearly observed on the sample from the bare tube. A large number of amorphous deposits are

Table 2. Elemental Compositions of the Coking Surfaces of Bare and TiO2-Coated Tubes (wt %)

| tube type  | Fe  | Cr  | S   | C   | Ti  | O   | Si  |
|------------|-----|-----|-----|-----|-----|-----|-----|
| bare       | 59.98 | 4.83 | 0.85 | 31.86 | 2.15 | 0.33 |     |
| TiO2-coated| 44.29 | 19.02 | 1.90 | 11.13 | 17.60 | 5.43 | 0.63 |
distributed around the filamentous carbon, and there are also some cobbles. No filamentous carbon is produced after passivation treatment (Figure 10b), and only amorphous and granular deposits are found. The diameters of the granular deposits are 30−150 nm. Therefore, 2000-cycle TiO₂ passivation treatment can effectively inhibit catalytic coking reactions and avoid the generation of filamentous carbon.

Figure 10. TEM images of coking morphologies on (a) bare and (b) TiO₂-coated tubes. Insets show higher magnification of selected areas.

Figure 11 shows the Raman spectra of the bare and TiO₂-coated tubes. Excitation using a 532 nm laser produced five peaks in the 1000−1700 cm⁻¹ region, which correspond to coke. Gaussian-fitted peaks of the Raman spectra are shown in Table 3. After passivation, the D3 peak is blue-shifted by 24 cm⁻¹ relative to that of the bare tube. No obvious difference is evident for the G peak position. The $I_{D3}/I_G$ value is 1.38 for the TiO₂-coated tube (Figure 11b), which is significantly smaller than that of the bare tube (2.28) because the graphitization degree of the carbon deposits after TiO₂ passivation is higher than that on bare tubes. The Raman spectra also exhibit broad signals in the 2000−3500 cm⁻¹ range, which are attributed to overtones and combinations of graphitic lattice vibration modes. For example, the ~2400 cm⁻¹ peak is assigned to the (2*D4) overtone.

Figure 11. Typical Raman spectra of coking on (a) bare and (b) TiO₂-coated tubes.

Table 3. Gaussian-Fitted Peaks of Raman Spectra (cm⁻¹)

| tube type      | D1 (cm⁻¹) | D2 (cm⁻¹) | D3 (cm⁻¹) | D4 (cm⁻¹) | G (cm⁻¹) | 2*D4 (cm⁻¹) | 2*D1 (cm⁻¹) | G + D1 (cm⁻¹) | 2*D2 (cm⁻¹) |
|----------------|-----------|-----------|-----------|-----------|----------|-------------|-------------|---------------|-------------|
| bare           | 1191      | 1338      | 1535      | 1596      | 1596     | 2443        | 2695        | 2922          | 3157        |
| TiO₂-coated    | 1188      | 1350      | 1559      | 1596      | 1596     | 2429        | 2709        | 2947          | 3173        |

Figure 12. Schematic diagram of coking mechanisms on (a) bare and (b) TiO₂-coated tubes.
2.4. Coking Mechanism. At the initial stage of coking, active metal elements on the inner surface of the bare tube catalyze cracking and produce fibrous carbon at the grain boundaries, as shown in Figure 12a. As the reaction proceeds, fibrous carbon continues to grow and entangle; it also adsorbs coking precursors from the air. The cracking reaction leads to increased pressure in the tube. This huge pressure presses the products into a compact layer. As carbon filaments entangle with each other and absorb more coking precursors, carbon deposition becomes more serious. High carbon deposition reduces the effective circulation diameter of the tube, and the system pressure drop increases. After passivation (Figure 12b), only the high-temperature cracking reaction occurs because the catalytic coking reaction is suppressed. The absence of filamentous carbon products weakens the surface adsorption of amorphous deposits, providing better anti-coking performance.

3. CONCLUSIONS
TiO2 thin films were prepared on a 316 substrate by ALD. The TiO2 films have an amonolot structure with a (101) preferential growth direction. Nano-indentation testing found that the 2000-cycle TiO2 thin film began to develop microcracks, so the 2000-cycle ALD was used for the steel tube passivation process. During the coking experiments, TiO2 coating of the tube reduced the pressure drop of the system but slightly increased the heat flux density. TiO2 thin film passivation treatment can reduce the diameter and number of granular deposits. It also reduces the degree of graphitization of the coking surface and the amount of activated carbon. Comparatively, no filamentous carbon is produced on the coking surface. TiO2 passivation treatment can inhibit the production of filamentous carbon; at the same time, amorphous deposition products and the carbon deposition rate are also greatly reduced.

4. EXPERIMENTAL DETAILS

4.1. Material Synthesis and Characterization. Stainless steel tube specimens with dimensions of Φ4 × 1 × 1200 mm were cut from a SS316 tube. Prior to film deposition, the tubes were sonicated in acetone and then alcohol for 10 min. ALD experiments were conducted in a flow reactor according to the scheme shown in Figure 13. When the tubes were placed in the reaction chamber, the precursor was introduced for reaction with the exposed inner walls of the tubes. The vacuum in the reaction chamber was 20 mTorr, and the pressure of the reactor outlet was stable at 364 mTorr when N2 was injected into the reaction chamber. To deposit TiO2 coatings, titanium tetraisopropanolate (TTIP, Nanjing Aimuyuan Scientific Equipment Co., 99.999%) and H2O2 (analytically pure, 25%) were alternatively pulsed in the reactor. TTIP was stored in stainless steel bottles and kept at 50 °C. The deposition temperature was fixed at 200 °C. One ALD cycle consisted of 1.5 s pulse of TTIP followed by 30 s pumping, 0.3 s of H2O2 exposure, and another 80 s pumping.

The crystal structure and thickness of TiO2 thin films deposited on Si(100) under the same conditions were studied. X-ray diffraction (XRD; D8 ADVANCE A25) was carried out at scattering angles of 20–80° using Cu Kα (λ = 0.15406 nm) radiation. Their morphology and composition were characterized by SEM (Gemini 500; acceleration voltage, 15 kV) equipped with an energy-dispersive X-ray spectrocope (EDS; OXFORD). The coking morphology was characterized by TEM, and Raman spectra were used to analyze the graphitization degree of the coking. An electronic analytical balance (precision, 0.0001 g) was used to weigh the masses of the coking tubes.

4.2. Anti-coking Performance Tests. Figure 14a shows the schematic of the anti-coking experiment conducted in the flow reactor. After fuel flowed out of the fuel tank, it was pressurized by a constant-flow pump. Mass flow was detected using a mass flowmeter before fuel entered the experimental section. The test reactor was fixed by copper plates on both sides, and alternating-current heating was applied. The reactor was equipped with thermocouples to measure temperature. Differential pressure sensors were installed at the inlet and outlet to detect pressure changes in the system. The pressure of the system was controlled using a Φ0.85 orifice plate. After the high-temperature fuel was cooled using a heat-exchange device, it was recycled in the waste tank. The temperature distribution of the test segment is presented in Figure 14b, as temperature is an important factor affecting fuel cracking and coking. The outlet was the hottest region.

Figure 15a shows the heat loss power of a copper plate calibrated with deionized water. The heat dissipation power was 210 W at 675 °C or higher. Figure 15b displays the temperature variation of the system with time. To reduce heat transfer deterioration, the temperature of the sample was maintained for 300 s above temperatures of 750 °C. The coking experiments were carried out at 800 °C at a flow rate of 1 m/s.
AUTHOR INFORMATION

Corresponding Author

Dayan Ma — State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, People’s Republic of China; orcid.org/0000-0001-8032-7385; Email: madayan@mail.xjtu.edu.cn

Authors

Changfa Zhu — State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, People’s Republic of China

Fei Ma — State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, People’s Republic of China; orcid.org/0000-0002-3911-7121

Zhenglei Dai — State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, People’s Republic of China; orcid.org/0000-0002-3709-8895

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05195

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was jointly supported by the National Natural Science Foundation of China (51671153 and 51771037), the Natural Science Foundation of Shaanxi Province (nos. 2019JM-028, 2019TD-020, and 2019JLM-30), and the Key Research and Development Project of Shandong Province (no. 2019GGX102023).

REFERENCES

(1) Yue, L.; Wu, J.; Gong, Y.; Hou, J.; Xiong, L.; Xiao, C.; Fang, W. Heat transfer and cracking performance of endothermic hydrocarbon fuel when it cools a high temperature channel. Fuel Process. Technol. 2016, 149, 112–120.

(2) Huang, H.; Spadaccini, L. J.; Sobel, D. R. Fuel-cooled thermal management for advanced aeroengines. J. Eng. Gas Turbines Power 2004, 126, 284–293.

(3) Jiang, R.; Liu, G.; Zhang, X. Thermal cracking of hydrocarbon aviation fuels in regenerative cooling microchannels. Energy Fuels 2013, 27, 2563–2577.

(4) Yin, K.; Mahamulkar, S.; Xie, J.; Shibata, H.; Malek, A.; Li, L.; Jones, C. W.; Agrawal, P.; Davis, R. J. Catalytic reactions of coke with dioxygen and steam over alkaline-earth-metal-doped cerium-zirconium mixed oxides. Appl. Catal., A 2017, 535, 17–23.

(5) Towfighi, J.; Sadrameli, M.; Niaei, A. Coke formation mechanisms and coke inhibiting methods in pyrolysis furnaces. J. Chem. Eng. Jpn. 2002, 35, 923–937.

(6) Abghari, S. Investigation of coke formation in steam cracking of atmospheric gasoil. J. Pet. Sci. Res. 2013, 2, 82–91.

(7) Mahamulkar, S.; Yin, K.; Agrawal, K.; Davis, R. J.; Jones, C. W.; Malek, A.; Shibata, H. Formation and oxidation/gasification of carbonaceous deposits: a review. Ind. Eng. Chem. Res. 2016, 55, 9760–9818.

(8) Gao, M.; Hou, L.; Zhang, X.; Zhang, D. Coke Deposition Inhibition for Endothermic Hydrocarbon Fuels in a Reforming Catalyst-Coated Reactor. Energy Fuels 2019, 33, 6126–6133.

(9) Ropital, F.; Broutin, P.; Reyniers, M. F.; Froment, G. F. Anticoking coatings for high temperature petrochemical reactors. Oil Gas Sci. Technol. 1999, 54, 375–385.

(10) Tang, S.; Shi, N.; Wang, J.; Tang, A. Comparison of the anticoking performance of CVD TiN, TiO₂ and TiC coatings for hydrocarbon fuel pyrolysis. Ceram. Int. 2017, 43, 3818–3823.

(11) Tang, S.; Liu, T.; Duan, S.; Guo, J.; Tang, A. Comparison of Growth Characteristics and Properties of CVD TiN and TiO₂ Anti-Coking Coatings. Processes 2019, 7, 574.

(12) Zhou, J.; Xu, H.; Luan, X.; Ling, X. Influence of the SiO₂/S coating and sulfur/phosphorus-containing coking inhibitor on coke formation during thermal cracking of light naphtha. Fuel Process. Technol. 2012, 104, 198–203.

(13) Pahtade, V. S.; Chavan, P. S.; Baisane, V. P. A review paper on vapour deposition coating. J. Eng. Appl. Sci. 2016, 3, 75–78.

(14) Brinker, C. J.; Hurd, A. J.; Schunk, P. R.; Frye, G. C.; Ashley, C. S. Review of sol-gel thin film formation. J. Non-Cryst. Solids 1992, 147-148, 424–436.

(15) Feng, H.; Elam, J. W.; Libera, J. A.; Setthapun, W.; Stair, P. C. Palladium catalysts synthesized by atomic layer deposition for methanol decomposition. Chem. Mater. 2010, 22, 3133–3142.

(16) Hui, L.; Li, J.; Gong, T.; Sun, D.; Lü, J.; Hu, S.; Feng, H. Fabrication of silica and Titania Anti-coking Passivation Layers in High Aspect-ratio Tubular Reactors by Atomic Layer Deposition. Chem. Res. Chin. Univ. 2019, 40, 201–209.

(17) Ma, Z.; Brown, S.; Howe, J. T.; Overbury, S. H.; Dai, S. Surface modification of Au/TiO₂ catalysts by SiO₂ via atomic layer deposition. J. Phys. Chem. C 2008, 112, 9448–9457.

(18) Feng, H.; Lu, J.; Stair, P. C.; Elam, J. W. Alumina over-coating on Pd nanoparticle catalysts by atomic layer deposition: Enhanced stability and reactivity. Catal. Lett. 2011, 141, 512–517.

(19) Pillai, S. C.; Periyat, P.; George, R.; McCormack, D. E.; Seery, M. K.; Hayden, H.; Colreavy, J.; Corr, D.; Hinder, S. J. Synthesis of...
high-temperature stable anatase TiO2 photocatalyst. J. Phys. Chem. C 2007, 111, 1605–1611.

(20) Chuang, L.-C.; Luo, C.-H.; Yang, S.-h. The structure and mechanical properties of thick rutile–TiO2 films using different coating treatments. Appl. Surf. Sci. 2011, 258, 297–303.

(21) Perry, A. J.; Pulker, H. K. Hardness, Adhesion and abrasion resistance of TiO2 films on glass. Thin Solid Films 1985, 124, 323–333.

(22) Niemela, J.-P.; Marin, G.; Karppinen, M. Titanium dioxide thin films by atomic layer deposition: a review. Semicond. Sci. Technol. 2017, 32, No. 093005.

(23) Bendavid, A.; Martin, P. J.; Takikawa, H. Deposition and modification of titanium dioxide thin films by filtered arc deposition. Thin Solid Films 2000, 360, 241–249.

(24) Mun, J.; Kim, S. W.; Kato, R.; Hatta, I.; Lee, S. H.; Kang, K. H. Measurement of the thermal conductivity of TiO2 thin films by using the thermo-reflectance method. Thermochim. Acta 2007, 455, 55–59.

(25) Blekkan, E. A.; Myrstad, R.; Olovik, O.; Rokstad, O. A. Characterization of tars and coke formed during the pyrolysis of methane in a tubular reactor. Carbon 1992, 30, 665–673.

(26) Kopinke, F. D.; Zimmermann, G.; Nowak, S. On the mechanism of coke formation in steam cracking—conclusions from results obtained by tracer experiments. Carbon 1988, 26, 117–124.

(27) Lahaye, J.; Badie, P.; Ducret, J. Mechanism of carbon formation during steamcracking of hydrocarbons. Carbon 1977, 15, 87–93.

(28) Sundaram, K. M.; Van Damme, P. S.; Froment, G. F. Coke deposition in the thermal cracking of ethane. AIChE J. 1981, 27, 946–951.

(29) Gong, T.; Hui, L.; Zhang, J.; Sun, D.; Qin, L.; Du, Y.; Li, C.; Lu, J.; Hu, S.; Feng, H. Atomic layer deposition of alumina passivation layers in high-aspect-ratio tubular reactors for coke suppression during thermal cracking of hydrocarbon fuels. Ind. Eng. Chem. Res. 2015, 54, 3746–3753.

(30) Bao, B.; Liu, J.; Xu, H.; Liu, B.; Zhang, W. Inhibitory effect of MnCr2O4 spinel coating on coke formation during light naphtha thermal cracking. RSC Adv. 2016, 6, 68934–68941.

(31) Cai, H.; Krzywicki, A.; Oballa, M. C. Coke formation in steam crackers for ethylene production. Chem. Eng. Process. 2002, 41, 199–214.

(32) Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman microspectroscopy of soot and related carbonaceous materials: spectral analysis and structural information. Carbon 2005, 43, 1731–1742.

(33) Cuesta, A.; Dhamelincourt, P.; Laureys, J.; Martínez-Alonso, A.; Tascon, J. M. D. Raman microprobe studies on carbon materials. Carbon 1994, 32, 1523–1532.