Nature Environment and Pollution Technology
An International Quarterly Scientific Journal
p-ISSN: 0972-6268
e-ISSN: 2395-3454
Vol. 18 No. 3 pp. 969-973 2019
Original Research Paper Open Access

Solid Reductant Based Selective Catalytic Reduction System for Exhaust Emission Control of Compression Ignition Engines

Caneon Kurien and Ajay Kumar Srivastava
Department of Mechanical Engineering, University of Petroleum and Energy Studies, Dehradun-248007, India

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 18-01-2019
Accepted: 04-02-2019

Key Words:
Catalytic reduction system
Exhaust emissions
Nitrates
Urea slip

ABSTRACT

Increasing concern over rising pollution levels in city limits has resulted in stringent emission regulations for automotive diesel engines. Exhaust emissions from diesel engines are composed of carbon monoxide, carbon dioxide, hydrocarbons, nitrates, soot particles and soluble organic faction. Post treatment, emission control technique including diesel oxidation catalysis system, diesel particulate filtration system and selective catalytic reduction system have been developed to reduce the emission levels from automotive engines to meet the latest emission norms. Selective catalytic reduction system, which is used for control of nitrate emission has to be intensified to bring down the emission levels as per the requirements for EURO VI and Bharat Stage VI emission norms. This paper provides a comprehensive overview on the post treatment exhaust emission control systems. A detailed literature survey has been conducted on the state of art nitrate emission control technologies including the use of alternate solid reactants for ammonia generation and catalysts for deNO$_x$ reactions, considering the adverse effects of byproducts released by these systems.

INTRODUCTION

Development of an effective after-treatment system for reducing the toxicity level of exhaust emissions from internal combustion engines has become a mandatory requirement for implementation of latest emission regulations like EURO VI and Bharat Stage VI (Misra et al. 2017, Caneon Kurien et al. 2018). For example, in India Bharat Stage IV emission norms have been enforced since April 2017 and it has been proposed to enforce Bharat Stage VI emission norms across the entire country by April 2020. The leap from BS IV to BS VI is very critical since the limit for particulate matter emission and nitrate (NO$_x$) emission from vehicles has to be brought down by an average of 73% and 76% for vehicles in all categories in the latest emission norm (Bose et al. 2018, Kurien & Srivastava 2018). Performance and durability of the existing emission control systems have to be improved to meet these stringent emission norms (Arthanareeswaren et al. 2015). Selective catalytic reduction based emission control system has proved to exhibit better NO$_x$ reduction efficiency compared to alternative techniques, and diesel particulate filtration (DPF) system with alternately plugged filter channels has the ability to trap the particulate matter emissions by significant amounts to meet these emission regulations (Bai et al. 2017). Integrated SCR and DPF system with catalyst coating in the particulate filter channels and provision for injection of aqueous urea before the inlet channels are commercially used for deNO$_x$ and particulate trapping applications (Kurien & Srivastava 2018). Schematic diagram on the working of the SCR system is shown in Fig. 1, where it can be seen that the exhaust gas stream with ammonia generated by hydrolysis of urea is introduced to the inlet channels of the substrate.

The soot particles present in the exhaust gas stream will accumulate in the porous wall by depth filtration and cake filtration, whereas catalysts embedded in the porous wall will speed up the reaction between ammonia and nitrates resulting in the production of nitrogen and water vapour at the outlet side of the channel (Kurien & Srivastava 2018). Various technical advancements have been included in the selective catalytic reduction technology since its commercial introduction in Europe in 2003 to provide better performance, broad temperature window and reasonable cost (Zhang et al. 2015). At the initial stages of development, SCR systems were used for removing 75% upward NO$_x$ and presently most countries rely on urea based SCR systems since it has the ability to reduce NO$_x$ emissions by more than 95% (Guan et al. 2014). A major challenge in the implementation of the emission control system is the simultaneous requirement for fuel and emission control (Falciglia et al. 2018). Various optimized combustion modes introduced in engines for improving fuel economy has a direct impact on the rise in raw NO$_x$ emissions. Hence, maintaining a balance between fuel economy requirement and NO$_x$ emission control is critical, since the improved combustion modes also reduces the temperature of exhaust gases below the catalyst light-off temperature for SCR system

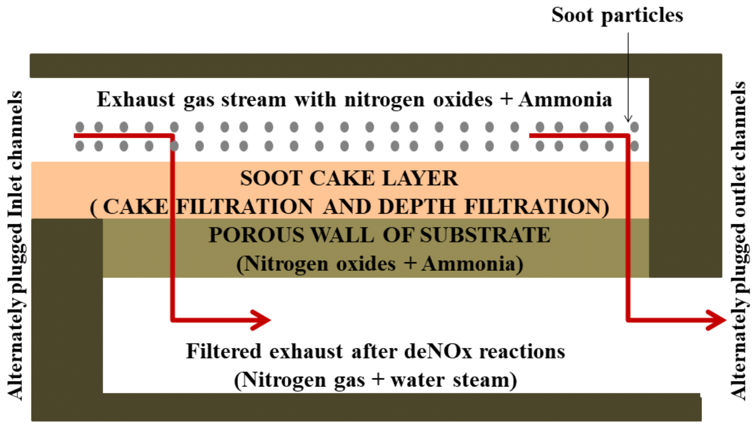

Fig. 1: Schematic diagram on the working of the SCR system in a pair of alternately plugged channels.

in cold start and low load conditions (Livingston et al. 2015). Development of catalysts with lower catalyst light-off temperatures would be the best alternative solution for achieving a trade-off between fuel economy and emission control (Bose et al. 2018).

Ammonia generation in urea based SCR system: Urea based SCR system uses an aqueous solution of urea which decomposes to ammonia in three stages when introduced to a stream of exhaust gas flow in an atomized form (Ting et al. 2018). At the initial stage when the aqueous solution is introduced to exhaust gas stream, water droplets present in the aqueous solution will evaporate resulting in the formation of molten urea as shown in Eq. 1. Molten urea will decompose to ammonia and isocyanic acid in a gaseous phase, which will undergo hydrolysis to produce ammonia and carbon dioxide over the catalyst present in SCR system as shown in Eqs. 2 and 3.

$$NH_2-CO-NH_2(aqueous) \rightarrow NH_2-CO-NH_2(molten) + H_2O(gas) \quad ...(1)$$

$$NH_2-CO-NH_2(molten) \rightarrow NH_3(gas) + HNCO(gas) \quad ...(2)$$

$$HNCO(gas) + H_2O(gas) \rightarrow NH_3(gas) + CO_2(gas) \quad ...(3)$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad ...(4)$$

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \quad ...(5)$$

$$4NH_3 + 5O_2 \rightarrow NO + 6H_2O \quad ...(6)$$

$$2NH_3 + 2NO_2 \rightarrow 4NH_4NO_3 + N_2 + H_2O \quad ...(7)$$

The overall reaction taking place during the hydrolysis of urea to ammonia is as shown in Eq. 3, where it can be seen that 2 moles of ammonia are generated by the hydrolysis of one mole of ammonia (Zhang et al. 2019). More than 90% of the nitrates present in the diesel exhaust are composed of nitrogen monoxide, hence it is considered for SCR reaction as shown in Eq. 4, where it can be seen that 4 moles of ammonia will react with 4 moles of nitrogen oxide in the presence of oxygen to produce 4 moles of nitrogen and 6 moles of water. The reaction will become slower in the absence of oxygen and alternately the rate of reaction will increase if equimolar amount of nitrogen monoxide and nitrogen dioxide is present in the exhaust stream (Baleta et al. 2017). Side reactions taking place in the SCR system include formation of nitrous oxide at temperatures higher than 400°C and undesirable reactions involving oxidation of ammonia to nitrogen monoxide might occur at temperatures higher than 500°C as shown in Eq. 5 and 6 (Guan et al. 2014). During low load conditions and cold start the exhaust gas temperature will be lower than 200°C leading to formation of ammonium nitrate (NH_4NO_3) which is undesirable as shown in Eq. 7.

Catalysts used in urea based SCR systems: Vanadium based SCR systems are used commercially owing to its higher temperature tolerance and resistance to sulphur poisoning (Huang et al. 2015). V-SCR system has been integrated to US Tier off highway exhaust after treatment systems considering its superior performance characteristics (Liu et al. 2019). Catalyst used in V-SCR system has anatase (titanium ore) as its base metal, onto which vanadium pentoxide and tungsten trioxide is impeded. SCR system is placed downstream of DPF system in exhaust emission control line and it has been observed that fuel based regeneration of the DPF would lead to deactivation of V-SCR catalyst. Toxic nature of vanadium compounds released at temperatures higher than 600°C has raised the requirement for development of alternate catalyst materials for SCR applications

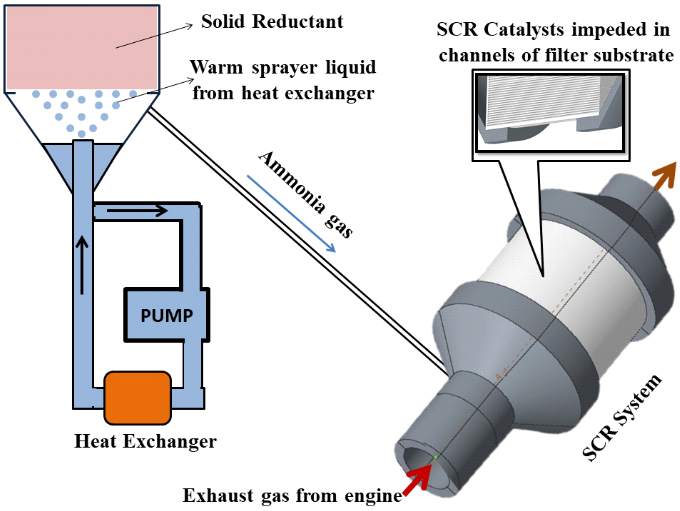

Fig. 2: Schematic diagram on the working of the solid reductant based SCR system.

(Zhang et al. 2017). Durability test of V-SCR system with silicon as thermal stabilizer at laboratory scale and full scale was conducted and the results showed that the catalyst has good durability and there was no release of vanadium compounds. Catalyst formulation by substituting vanadium pentoxide with rare earth ferrous vanadate exhibited good NO_x conversion efficiency at lower temperatures and is thermally stable up to 850°C without any degradation (Yang et al. 2018). Zeolite based SCR catalysts supported with base transition metals like iron and copper are used in the applications where combination of DPF system and SCR catalysts are applied to meet stringent emission norms (Hosokawa et al. 2017). Copper zeolite and iron zeolite catalysts have good performance characteristics at high space velocities and thermal stability. Copper zeolite and iron zeolite based SCR catalysts exhibit good $deNO_x$ performance at lower temperatures and has good durability at higher temperature. A comparative study on the thermal aging of the vanadium, copper zeolite and iron zeolite catalysts was conducted, and it showed that vanadium based catalysts deactivated at higher temperatures which is required for DPF regeneration (Xu et al. 2018). Hydrothermal aging of the copper and iron zeolite based catalysts is another major challenge leading to degradation of catalysts by dealumination and thermal collapse. Some other factors, which affect the service life of selective catalytic reduction system include sulphur poisoning, hydrocarbon poisoning and platinum-palladium poisoning (Miyahara et al. 2008).

Release of byproducts from urea based SCR system and their control: In common practice, the deNOx efficiency of the SCR system is improved by overdosing the urea, which will increase the risk of urea slip from SCR system. Ammonia slip in exhaust side is controlled by the application of ammonia slip catalyst (ASC) for the oxidation of ammonia to nitrogen gas and ASC is made mandatory in EURO VI and US 2010 regulations. Undesired reactions leading to the formation of nitrogen dioxide and nitrous oxide can be controlled by making sure that the ASC catalyst has high activity and selectivity for a wide range of operating temperatures which was developed by using accelerated progressive catalyst as tool (Kamasamudram et al. 2011). Nitrous oxide (N_2O) gas generated as byproduct of undesired reactions taking place in the SCR system is considered as a regulated greenhouse gas which has 298 times higher global warming potential than carbon dioxide. Nitrous oxide formation is observed to occur at temperatures lower than 250°C and also at temperatures higher than 500°C due to oxidation of NO and O_2 as shown in Eqs. 8 and 9.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad ...(8)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad ...(9)$$

Iron zeolite based SCR catalysts are found to be effective in abatement of nitrous oxide by decomposition of nitrous oxide to nitrogen but not in a broad temperature window. The most adopted method for controlling the nitrous oxide formation includes optimization of catalyst formulation and operation strategies so that the formation of nitrous oxide can be prevented.

Ammonia generation from solid reductants: Commercially available SCR systems work by injection of urea (aqueous solution) to the exhaust gas stream for the generation of ammonia by hydrolysis reactions. Some of the properties of urea like corrosive nature, lower freezing point and tendency to decompose at temperatures above 50-60°C have raised the need for development of an alternate technique for the generation of ammonia in SCR system (Zhang et al. 2015). Also the generation of ammonia from urea would also vary depending on the engine operating modes and exhaust conditions; hence it is very complicated to design a system for generating uniform concentration of ammonia. Also the temperature window for operation of the SCR system has been narrowed by the urea based ammonia generation since the hydrolysis reactions are difficult to occur at temperatures below 200°C. The exhaust gas temperature during urban range is found to be below 200°C, hence injection of aqueous urea during these operating conditions will result in production of undesired byproducts. All these limitations for operation of SCR system can be overcome if a system for injection of ammonia gas can be developed since it will broaden the operating temperature window and also production of undesirable products can be avoided (Huang et al. 2015). Major properties that decide the application of solid reactants for generation of ammonia gas include its volumetric efficiency, mass efficiency and ammonia release temperatures. Some of the solid reactants, which have the ability to generate ammonia gas, include solid urea, ammonium salts and metal ammine chlorides. Ammonium salts like ammonium carbamate and ammonium carbonate can be decomposed to release ammonia gas in two steps with reference to the thermogravimetric analysis performed, where it was observed that ammonium carbamate decomposes readily at low temperature. Two stage decomposition reaction of ammonium carbamate is as shown in Eqs. 10 and 11.

Metal ammines have complex coordination structure in which ammonia forms ligand bond with the central metal cation and ammonia generation from these depends on the coordination sites of ammonia molecules. Metal ammines like magnesium ammine chloride, strontium ammine chloride and calcium ammine chloride releases ammonium molecules in multi-step process upon heating, where molecules attached to the equatorial sites are released first followed by the molecules attached to the apical sites (Carder et al. 2017). Three step process involved in the release of ammonium molecules from calcium ammine chloride is as shown in Eqs. 12 to 14, where a total number of 8 ammonium molecules are released during the overall reaction. Replacement of the aqueous urea solution commercially known as adblue Diesel Exhaust Fluid (DEF) with the solid reductants would be the most possible alternative for improving the $deNO_x$ efficiency at broader temperature range.

$$NH_4COONH_2 \leftrightarrow NH_3 + HCOONH_2 \quad ...(10)$$

$$HCOONH_2 \leftrightarrow NH_3 + CO_2 \quad ...(11)$$

$$Ca(NH_3)_8Cl_2 \leftrightarrow Ca(NH_3)_2Cl_2 + 6NH_3 \quad ...(12)$$

$$Ca(NH_3)_2Cl_2 \leftrightarrow CaNH_3Cl_2 + NH_3 \quad ...(13)$$

$$CaNH_3Cl_2 \leftrightarrow CaCl_2 + NH_3 \quad ...(14)$$

Solid reductant based SCR system would require a closed container setup like reactor where warm liquid at a temperature around 60°C has to be sprayed onto the solid reductant for decomposition of the reductant to produce ammonia gas. The sprayer liquid has to be pumped back to the reservoir and recirculated, hence working as closed system (Schott et al. 2012). The ammonia gas released from the reactor is directed to the exhaust flow line via gas flowmeter where the flow rate of the gas injected can be varied accordingly. Schematic concept diagram of the solid reductant based SCR system is as shown in Fig. 2. Solid reductant based SCR system using ammonium carbamate for ammonia generation was developed, where the results showed that ammonium carbamate released sufficient amount of ammonia gas producing an overall conversion efficiency of 80-90% in the SCR system of pick-up truck. Ammonium carbamate decomposes to ammonia at a temperature of 60°C, which is achieved by spraying of heat transfer fluid onto the solid reductant (Bai et al. 2017). Pressure inside the reactor system will rise as the generation of ammonia gas continues and it is introduced to the exhaust flow stream via dosage control valve. Dosage of the ammonia gas will vary depending on the operating mode of the engine. Threat of urea slip and undesired deposits during cold start and low load conditions can be eliminated completely by introduction of solid reductant based SCR system (Cao & Jiang 2016). Ammonia density of the solid reductants is also higher, hence the reactor will be compatible with the exhaust line and also ensure longer range of service life (Chen et al. 2012).

CONCLUSIONS

Selective catalysis reduction based emission control system is a mandatory external attachment for meeting the emission regulations like US 2010 and EURO VI. Urea based SCR system with catalyst coating of copper or iron zeolite is commercially available SCR technique, but the occurrence of undesired reactions leading to release for more toxic byproducts has led to the development of alternate $deNO_x$ techniques. Solid reductant based SCR system is observed to be an effective alternative for ammonia generation as compared to urea based SCR systems. Ammonium salts like ammonium carbamate and ammonium carbonate have the ability to generate ammonia for about 80-90% NO_x conversion for small, light and medium duty diesel engine applications. Undesired reactions occurring in urea based SCR systems during cold start and cold transient cycles can be rectified by introduction of SSCR systems which will also reduce the deposit risks. Performance of SCR system can be enhanced by using solid reductants for ammonia generation owing to its higher ammonia generation density hence the refill interval can be extended.

REFERENCES

Arthanareeswaren, G. and Varadarajan, K.N. 2015. CFD study on pressure drop and uniformity index of three cylinder LCV exhaust system. Procedia Engineering, 127: 1211-1218.

Bai, S., Chen, G., Sun, Q., Wang, G. and Li, G.X. 2017. Influence of active control strategies on exhaust thermal management for diesel particular filter active regeneration. Applied Thermal Engineering, 119: 297-303.

Baleta, J., Martinjak, M., Vujanovic, M., Pachler, K., Wang, J. and Duic, N. 2017. Numerical analysis of ammonia homogenization for selective catalytic reduction application. Journal of Environmental Management, 203: 1047-1061.

Bose, D., Kandpal, V., Dhawan, H., Vijay, P. and Gopinath, M. 2018. Energy recovery with microbial fuel cells: Bioremediation and bioelectricity. In: Waste Bioremediation, Springer, Singapore, pp. 7-33.

Bose, D., Kurien, C., Sharma, A., Sharma, S. and Sharma, A. 2018. Low cost cathode performance of microbial fuel cell for treating food wastewater. Nature Environment and Pollution Technology, 17(3): 853-856.

Cao, Erming and Jiang, Kai 2016. Neurocomputing adaptive unscented Kalman Fi Lter for input estimations in diesel-engine selective catalytic reduction systems. Neurocomputing, 1-7.

Carder, D., Ryskamp, R., Besch, M. and Thiruvengadam, A. 2017. Emissions control challenges for compression ignition engines. Procedia IUTAM, 20: 103-111.

Chen, Y., Peng, W., Wang, S., Zhang, F., Zhang, G. and Fan, X. 2012. Supported nano-sized gold catalysts for selective reduction of 4, 4'-dinitrostilbene-2, 2'-disulfonic acid using different reductants. Dyes and Pigments, 95(2): 215-220.

Falciglia, P.P., Roccaro, P., Bonanno, L., De Guidi, G., Vagliasindi, F.G. and Romano, S. 2018. A review on the microwave heating as a sustainable technique for environmental remediation/detoxification applications. Renewable and Sustainable Energy Reviews, 95: 147-170.

Guan, B., Zhan, R., Lin, H. and Huang, Z. 2014. Review of state of the art technologies of selective catalytic reduction of NOx from diesel engine exhaust. Applied Thermal Engineering, 66(1-2): 395-414.

Hosokawa, S., Matsuki, K., Tamaru, K., Oshino, Y., Aritani, H., Asakura, H., Teramura, K. and Tanaka, T., 2017. Selective reduction of NO over Cu/Al_2O_3: Enhanced catalytic activity by infinitesimal loading of Rh on Cu/Al_2O_3. Molecular Catalysis, 442: 74-82.

Huang, H., Jiang, B., Gu, L., Qi, Z. and Lu, H. 2015. Promoting effect of vanadium on catalytic activity of Pt/Ce-Zr-O diesel oxidation catalysts. Journal of Environmental Sciences, 33: 135-142.

Kamasamudram, K., Yezerets, A., Chen, X., Currier, N., Castagnola, M. and Chen, H.Y. 2011. New insights into reaction mechanism of selective catalytic ammonia oxidation technology for diesel aftertreatment applications. SAE International Journal of Engines, 4(1): 1810-1821.

Kurien, C. and Srivastava, A.K. 2018. Advancement in the design of automotive catalytic filter for meeting environmental emission norms. Nature Environment and Pollution Technology, 17(2): 433-438.

Kurien, C. and Srivastava, A.K. 2018. Active regeneration of diesel particulate filter using microwave energy for exhaust emission control. Advances in Intelligent Systems and Computing, 624: 1233-1241.

Kurien, C. and Srivastava, A.K. 2018. Geometrical modelling and analysis of automotive oxidation catalysis system for compliance with environmental emission norms. Nature Environment and Pollution Technology, 17(4): 1207-1212.

Kurien, C., Srivastava, A.K. and Naudin, J., 2018. Modelling of regeneration and filtration mechanism in diesel particulate filter for development of composite regeneration emission control system. Archive of Mechanical Engineering, 65(2): 277-90.

Liu, Y., Tursun, M., Yu, H. and Wang, X. 2019. Surface property and activity of Pt/Nb_2O_5-ZrO_2 for selective catalytic reduction of NO by H_2. Molecular Catalysis, 464: 22-28.

Livingston, P., Lee, C.S.J. and Nguyen, D. 2015. Creation and third-party verification of large governmental greenhouse gas emission report. Strategic Planning for Energy and the Environment, 34(3): 43-62.

Misra, A., Panchabikesan, K., Ayyasamy, E. and Ramalingam, V. 2017. Sustainability and environmental management: Emissions accounting for ports. Strategic Planning for Energy and the Environment, 37(1): 8-26.

Miyahara, Y., Takahashi, M., Masuda, T., Imamura, S., Kanai, H., Iwamoto, S., Watanabe, T. and Inoue, M., 2008. Selective catalytic reduction of NO with C1-C3 reductants over solvothermally prepared Ga_2O_3-Al_2O_3 catalysts: Effects of water vapor and hydrocarbon uptake. Applied Catalysis B: Environmental, 84(1-2): 289-296.

Schott, F.J., Steigert, S., Zuercher, S., Endisch, M. and Kureti, S. 2012. Reactor design for the evaluation of diesel oxidation catalysts supported by sintered metal filters. Chemical Engineering and Processing: Process Intensification, 62: 54-58.

Ting, A.W.L., Harold, M.P. and Balakotaiah, V. 2018. Elucidating the mechanism of fast cycling NOx storage and reduction using C_3H_6 and H_2 as reductants. Chemical Engineering Science, 189: 413-421.

Xu, W., Zhang, G., Chen, H., Zhang, G., Han, Y., Chang, Y. and Gong, P. 2018. Mn/beta and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: Effect of manganese precursors. Chinese Journal of Catalysis, 39(1): 118-127.

Yang, J., Chang, Y., Dai, W., Wu, G., Guan, N. and Li, L. 2018. Bimetallic Cr-In/H-SSZ-13 for selective catalytic reduction of nitric oxide by methane. Chinese Journal of Catalysis, 39(5): 1004-1011.

Zhang, H., Wang, J. and Wang, Y.Y., 2015. Removal of NOx sensor ammonia cross sensitivity from contaminated measurements in Diesel-engine selective catalytic reduction systems. Fuel, 150: 448-456.

Zhang, M., Huang, B., Jiang, H. and Chen, Y. 2017. Research progress in the SO_2 resistance of the catalysts for selective catalytic reduction of NOx. Chinese Journal of Chemical Engineering, 25(12): 1695-1705.

Zhang, S., Liu, S., Hu, W., Zhu, X., Qu, R., Wu, W., Zheng, C. and Gao, X. 2019. New insight into alkali resistance and low temperature activation on vanadia-titania catalysts for selective catalytic reduction of NO. Applied Surface Science, 466: 99-109.