Studies of the interaction between diesel soot and SrTiO₃ – based catalysts

B. Ura³, M.J. Illán-Gómez², A. Bueno-López², F. E. López-Suárez², J. Trawczyński³, H. Grothe¹

¹Institute of Materials Chemistry, Vienna University of Technology, Veterinarplatz 1/GA, A-1210 Vienna, Austria

²Universidad de Alicante, Facultad de Ciencias, Av. Alicante s/n. San Vicente del Raspeig, 03080 Alicante, Spain

³Wroclaw University of Technology, Division of Chemistry and Technology Fuels, Gdanska 7/9, 50-344 Wroclaw, Poland

Introduction

Diesel engines possess the advantages of lower fuel consumption and lower emissions of CO₂, CO and hydrocarbons (HC) compared to gasoline fueled engines. However, exhaust gasses from diesel engines contain larger amounts of NO_x and soot. Particulate emissions from these engines are one of the most dangerous air pollutants and can be harm to human health. Law regulations concerning diesel soot particulates and NO_x emissions demand developing new effective method of exhaust gases purification. One such method is the filtration on a porous trap followed by burning out trapped particulates. In absence of catalyst, filters must attain temperatures of at least 600-650°C (in air) in order to auto-ignite deposited soot and sustain the combustion. Temperatures of exhaust gasses are usually much lower and external heating is needed. The regenerating of soot filters may be assisted by catalytic combustion. The role of the catalyst is to lower the temperature of this process [1, 2]. Mixed oxides with the general formula ABO₃ and perovskite-like structures have been studied widely in view of their activity in complete oxidation, thermal stability and relatively low costs. Due to these properties perovskites are often suggested as a substitute for noble metals in catalytic combustion of VOC, HC and CO. Among the perovskites, those structures containing both, cations of transition metals and rare earth metals, are of increasing interest for catalytic purification of automotive exhaust gases [2-5]. Carbon-oxygen functionalities (COF) on the soot surface are formed by reaction with oxidizing exhaust gases. The nature and amount of COF are affected among others, by soot surface, particle size, temperature, type of the oxidizing medium (gas or liquid) and in the case of catalytic oxidation - specific properties of catalyst and type of contact between soot and catalyst. When heated in helium, COF decompose into CO and CO₂. In case of activated carbons signals of CO₂ and can be attributed to the decomposition of carboxylic (anhydride) or lactonic groups (my own Carbon reference?). Signals of CO are attributed for decomposition of quinonic or phenolic groups [6]. Three mechanisms of oxidation were proposed for catalytic soot oxidation: a redox mechanism (involving surface or lattice oxygen associated with metal oxides), a spill-over mechanism (involving adsorbed surface oxygen producing carbon surface COF) and a push-pull mechanism [7]. It is believed that weakly adsorbed surface oxygen contributes to the soot combustion over perovskite-type catalysts by a spill-over mechanism [8]. Especially under

conditions of loose contact between soot and catalyst the spill-over mechanism might play a predominant role.

The present work aims to investigate the mechanisms of the reaction between soot and Sr titanates with perovskite like structure in the environment containing oxidizing agents. In the series of $Sr_{1-x}M_xTiO_3$ (x = 0 or 0.2; M = K, Cs) mixed oxides with perovskite-like structure, exhibiting deficient of positive charge (resulting from partial substitution of strontium by alkali metal) is balanced by formation of oxygen vacancies. Adsorption and activation of molecular oxygen or NOx on the vacancies should improve catalytic activity of the materials in oxidation of soot.

Experimental part

Samples of SrTiO₃, Sr_{0.8}K_{0.2}TiO₃ and Sr_{0.8}Cs_{0.2}TiO₃ were prepared by the citrate solgel method starting from H_2O_2 , citric acid, titanium(IV) isopropylate and aqueous solutions of corresponding metals nitrates. The solvents were evaporated from precursor's mixtures at 90°C. The remaining viscous syrup was dried and solid products were calcined in air at 850°C for 6h.

About 50 mg of either pure soot (Printex U® is a color gas black with primary particle diameter of 25 nm and a BET surface of about 100 m² g⁻¹. It is manufactured by the Evonik Degussa AG) or a mixture of soot and catalyst (ratio 1:5, loose contact) was placed inside a quartz reactor and was used for TPD-MS experiments. Runs were performed under high vacuum conditions (10^{-5} mbar) and at elevated temperatures of up to 900°C with a rate of 10 K min⁻¹. The measured molecular fragments were: CO₂ (M⁺ = 44 m/e), CO (M⁺ = 28 m/e), OH (M⁺ = 17 m/e), NO (M⁺ = 30m/e) and NO₂ (M⁺ = 46 m/e). After heating the sample, it was cooled down to room temperature and NO₂ and/or O₂ were absorbed. A mixture of 3000 ppm NO₂ in 24.8 mbar oxygen was chosen and the sample was kept at 400°C during the reaction. After 40 minutes the sample was cooled to room temperature, the gas was pumped off, the pressure was stabilized (5-6 x 10 ⁻⁵ mbar) and a TPD-MS experiment was performed.

Results and discussion

Fig. 1 shows the TPD-MS profiles of the mass $M^+ = 44$ m/e desorbed from studied materials. Raw SrTiO₃ (without soot and adsorbed gasses) evolves CO₂ at 300°C and 850°C. The signal at 300°C can be attributed to the decomposition of surface carbonates and the one at 850°C to the decomposition of bulk strontium carbonate. XRD patterns of SrTiO₃ (not presented here) confirm the presence of small amounts of SrCO₃ in the catalyst material. The adsorption of NO₂ on the mixture of SrTiO₃ with soot (SrTiO₃ + soot + NO₂) produces signals at 400°C; 530°C and 785°C. The sample (SrTiO₃ + soot + O₂) exhibits only one signal at 740°C.



Fig. 1. TPD-MS curves of: $\mathbf{a} - SrTiO_3$; $\mathbf{b} - Sr_{0.8}K_{0.2}TiO_3$; $\mathbf{c} - Sr_{0.8}K_{0.2}TiO_3$ (scale 0-5) $\mathbf{d} - Sr_{0.8}Cs_{0.2}TiO_3$. Recorded mass: 44

Partial substitution of strontium by potassium significantly lowers the temperature at which the CO₂ signals are observed (Fig. 1b). Raw $Sr_{0.8}K_{0.2}TiO_3$ shows a pattern with an intense and sharp peak at about 150°C and a broad signal at ~650°C. Adsorption of NO₂ and O₂ on $Sr_{0.8}K_{0.2}TiO_3$ results in the CO₂ desorption pattern which posses three maxima. Somewhat different TPD patterns are observed in the case of $SrTiO_3$ partially substituted with cesium. All samples show a CO₂ signal at ca 700-790°C. Raw $Sr_{0.8}Cs_{0.2}TiO_3$ shows only one peak CO₂ at 790°C. The largest amount relative of CO₂ is desorbed from sample ($Sr_{0.8}Cs_{0.2}TiO_3 + \text{soot} + NO_2 + O_2$). Two peaks are shown at 405 and 740°C.

Fig. 2 shows the TPD-MS profiles for m/e = 28 (CO). The sample of (SrTiO₃ + soot) produces a broad signal of CO with maximum at 780°C; adsorption of either N₂ or (O₂ + NO₂) on the mixture (SrTiO₃ + soot) results in he CO profiles with maximums respectively at 150°C and 740°C. The mixture of (Sr_{0.8}K_{0.2}TiO₃ + soot) produce desorption band with peak at 148°C and two overlapping peaks at 650°C and 740°C. Adsorption of oxygen on this mixture (Sr_{0.8}K_{0.2}TiO₃ + soot + O₂) results in desorption signal at 725°C; adsorption of NO₂ produces two signals (365°C and 725°C); after adsorption of (O₂ + NO₂) on this mixture (Sr_{0.8}K_{0.2}TiO₃ + soot + O₂ + NO₂) there are no signals corresponding to m/e = 28.



Fig. 2. TPD-MS curves of: $\mathbf{a} - SrTiO_3 \mathbf{b} - Sr_{0.8}K_{0.2}TiO_3 \mathbf{c} - Sr_{0.8}Cs_{0.2}TiO_3 - recorded m/e = 28$

Fig.3 presents the TPD-MS patterns for m/e = 30 (NO) of studied materials. The sample of (SrTiO₃ + NO₂) shows large, sharp signal at temperature 478°C. It is difficult to explain a presence of this signal – it might be supposed that NO₂ chemisorbed on anionic vacancies of SrTiO₃ partially decomposes yielding NO. This supposition is confirmed by signal of O₂ (m/e =32) desorption (not presented here) at 480°C. NO₂ adsorbed on the mixture (SrTiO₃ + soot) produce NO signal at 360°C. Incorporation of alkali metal into SrTiO₃ structure increases its adsorptive capacity towards NO₂. The presence of soot lowers a temperature at which signal of m/e = 30 appears – this effect is more pronounced for potassium doped SrTiO₃ than for Cs-doped one. Adsorbed species partially decompose under experimental conditions producing NO and O₂ results of the studies are summarized in Tab. 1.

Sample	NO, m/e=30	O ₂ , m/e=32	CO, m/e=28	CO ₂ , m/e=44
SrTiO ₃	_	_	_	855
$Sr_{0.8}K_{0.2}TiO_3$	_	_	_	170;650
$Sr_{0.8}Cs_{0.2}TiO_3$	_	_	_	790
SrTiO ₃ +NO ₂	480	480	_	_
Sr _{0.8} K _{0.2} TiO ₃ +NO ₂	625	625	_	_
Sr _{0.8} Cs _{0.2} TiO ₃ +NO ₂	535	520	_	_
SrTiO ₃ +soot+NO ₂	360	480	360; 735	530; 785
Sr _{0.8} K _{0.2} TiO ₃ +soot+NO ₂	360	360	360; 725	375; 525
Sr _{0.8} Cs _{0.2} TiO ₃ +soot +NO ₂	715	715	750	715
SrTiO ₃ +soot+O ₂	_	_	720	740
$Sr_{0.8}K_{0.2}TiO_3$ +soot +O ₂	_	_	725	395
Sr _{0.8} Cs _{0.2} TiO ₃ +soot +O ₂	_	_	765	725
SrTiO ₃ +soot+NO ₂ +O ₂	490	490	725	770
$Sr_{0.8}K_{0.2}TiO_3$ +soot +NO ₂ +O ₂	480	_	695	475
$Sr_{0.8}Cs_{0.2}TiO_3$ +soot +NO ₂ +O ₂	735	735	775	405; 740

Tab. 1. Temperatures (in °C) at which the maxima in the TPD-MS curve appear





b





Fig. 3. TPD-MS curves of: $\mathbf{a} - SrTiO_3 \mathbf{b} - Sr_{0.8}K_{0.2}TiO_3 \mathbf{c} - Sr_{0.8}Cs_{0.2}TiO_3 - recorded masses - 30$

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