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Review

Simultaneous oxidation of carbon black and volatile organic compounds over Ru/CeO_2 catalysts

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ABSTRACT

Ru/CeO_2 catalysts with Ru loading of 1–5 wt.% were prepared by wet impregnation from aqueous ruthenium (III) nitrosyl nitrate solution and activation with an air flow at 600 °C for 4 h. This activation resulted in a considerable reactivity for the catalytic oxidation of carbon black (CB) ($T_{50\%}$ ~350 °C "tight contact" mixtures and $T_{50\%}$ ~515 °C "loose contact" mixtures) and volatile organic compounds (VOCs) ($T_{50\%}$ = 175 °C for propene, $T_{50\%}$ = 215 °C for toluene). When carbon black oxidation was conducted under "propene (6000 ppm) + air" or "toluene (2000 ppm) + air" flow, the elimination of an important part of CB was observed at relatively low temperatures comparing to its elimination under pure air flow. These temperatures correspond to the total oxidation of the VOC present in the reactant gases. Carbon black total elimination was also investigated under isotherm conditions in the presence and in the absence of propene. Total elimination occurred during shorter times when combustion was performed under propene. TPR study showed that ruthenium species present in the catalysts after activation reduces at relatively low temperatures (<100 °C) and that from a Ru loading of 1.5 wt.%, agglomerated ruthenium oxide was formed and that this latter is more difficult to reduce (>100 °C).

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1. Introduction

Reducing the particulate matter (PM) and volatile organic compounds (VOCs) emissions simultaneously has been a major challenge for car manufacturers and researchers. In fact, in several cases, VOCs emissions are accompanied by carbon particulates emissions. The most known example is that of diesel engines [1–3], but many industries are also sources of particulate and volatile emissions [4]. Emission control strategies include changes and improvements in the fuel used, engine or process modifications or exhaust after-treatment systems. These latter provide satisfactory results for compliance with the emission regulations where the engine or process modifications or fuel improvements are not sufficient. Using oxidation catalysts in order to oxidize carbonaceous particulates is one of the promising after-treatment systems. These catalysts also provide significant reductions in the carbon monoxide (CO) and hydrocarbons (HC) emissions.

In literature, different laboratory experiments were performed to study the combustion of soot particulates. In some of it, carbon black (CB) oxidation was studied under isothermal conditions and in others “CB + catalyst” mixtures were subjected to a dynamic temperature increase. Reactant gases ranged from synthetic air [5] to mixtures of different gases “O_2, NO, H_2O, SO_2, N_2...” [6,7].

Ruthenium oxide catalysts have been demonstrated to be reactive in acetic acid [8], propene [9] and carbon black [10,11] oxidation reactions. The pronounced reactivity of ruthenium oxide catalysts seems to result from the reducibility of the oxide itself. In the presence of another reducible oxide such as ceria (CeO_2), the oxygen needed for the oxidation reaction was reported to be provided by the second oxide.

In this paper, the simultaneous oxidation of carbon black and volatile organic compounds over Ru/CeO_2 catalysts is investigated.

2. Experimental

2.1. Synthesis of Ru/CeO_2 catalysts

Cerium hydroxide $Ce(OH)_4$ was precipitated from cerium (III) nitrate hexahydrated solution $Ce(NO_3)_3 \cdot 6H_2O$ 0.25 M and a sodium hydroxide alkali solution NaOH 1 M. The resulting hydroxide $Ce(OH)_4$ was filtered, washed and dried overnight in a drying oven at 100 °C, then it was calcined at 500 °C to obtain ceria CeO_2. Different volumes of ruthenium (III) nitrosyl nitrate $Ru(NO)(NO_3)_3$ solution have been impregnated on ceria in order to obtain solids with different loadings of ruthenium (1, 1.5, 1.65, 1.85, 2, 3, 5 wt.%). These solids have been designated as RuxCe (x stands for the Ru wt.%). After drying at 100 °C for about 20 h, they were stabilized by calcination under dried air at 600 °C for 4 h.

2.2. Catalytic tests

The catalytic test towards the combustion of carbon black (CB) (N330 DEGUSSA: specific surface area $S_{sp} = 76\ m^2\ g^{-1}$, elementary analysis: 97.23 wt.% C; 0.73 wt.% H; 1.16 wt.% O; 0.19 wt.% N; 0.45 wt.% S) was studied by simultaneous thermogravimetric (TG) – differential scanning calorimetry (DSC) analysis with NETZSCH STA 409 apparatus. Before test, 10 wt.% of CB and 90 wt.% of catalyst were mixed slightly in an appropriate cell for 10 min (“loose contact”) or heavily in a ball miller for 40 min (“tight contact”). Thirty milligrams of the mixture were then loaded in an alumina crucible and heated from room temperature up to 1000 °C (5 °C min^{-1}) under air flow of 75 mL min^{-1}.

The propene (C_3H_6; 6000 ppm) and toluene (C_7H_8; 2000 ppm) oxidations were carried out in a catalytic micro-reactor coupled to a Varian 3600 gas chromatograph using a double detection FID and TCD. Hundred milligrams of the catalyst were tested in the presence of the different VOCs (air + VOC = 100 mL min^{-1} – 1 °C min^{-1}).

The propene/toluene and carbon black simultaneous oxidation was studied using the previous two techniques. Concerning DSC/TG technique, the experimental design was kept unchanged but a fixed amount of propene was introduced into reactant gases flow. The total flow was also increased from 75 mL min^{-1} to 100 mL min^{-1} for comparison reasons. The second technique coupled a catalytic micro-reactor to a Varian 4900 micro-gas chromatograph. This latter allowed consecutive automatic injections separated by relatively short time periods (120 s for propene test and 90 s for toluene test). Thus, several points corresponding to the combustion of carbon black in the presence of a VOC were recorded. Hundred milligrams of the catalyst mixed to 10 wt.% of CB were tested in the presence of propene/toluene (air + propene = 100 mL min^{-1}; 6000 ppm of propene or air + toluene = 100 mL min^{-1}; 2000 ppm of toluene – 1 °C min^{-1}). For isothermal studies, catalyst/CB mixtures were heated from room temperature till the isotherm temperature (1 °C min^{-1}). Initial time ($t = 0$) corresponds to the beginning of heating under reactant gases flow. Thus CB conversion begins before the isotherm settlement. The micro-reactor is loaded with a 111 mg of the mixture in a way to have a constant catalyst quantity (100 mg). After reaching the desired isotherm duration, the micro-reactor is rapidly cooled (to stop the reaction) and the recovered mixture is analysed by TG apparatus to determine remaining CB quantity.

2.3. Characterization of the solids

2.3.1. BET and elemental analysis

The specific surface areas (S_{sp}) were measured based on BET method using an ANKERSMIT Quanta Sorb Junior apparatus. Calcined samples are treated at 130 °C under nitrogen flow for 15 min. The adsorption of a “30% N_2 (adsorbed gas) + 70% He (carrier gas)” mixture is then carried at −196 °C. After the completion of adsorption, the sample is removed from liquid nitrogen and leaved at room temperature. This quick heating of the sample desorbs the gaseous nitrogen which is quantized using a thermal conductibility detector. Specific surface areas are given in Table 1.

Elementary analyses were performed on the calcined solids and element weight percentages are given in Table 1.

2.3.2. XRD analysis

The XRD experiments were performed at ambient temperature on a BRUKER D8 Advance diffractometer using CuKα radiation (1.5405 Å), which components are subtracted from the rough spectrum. The scattering intensities were measured over an angular range of $20^\circ < 2\theta < 60^\circ$ for all the samples with a step-size of $(2\theta) = 0.02^\circ$. The diffraction patterns have been indexed by comparison with the JCPDS files.

Table 1
Specific surface areas (S_{sp}) and elementary content (m%) of the solids.

Sample	S_{sp} ($m^2\ g^{-1}$)	Ru (m%)	Ce (m%)	O (m%)
CeO_2	93	–	–	–
RuO.67Ce	89	0.56	77.51	21.93
Ru1Ce	86	0.85	76.85	22.3
Ru1.5Ce	82	1.31	78.71	19.98
Ru2Ce	78	1.79	77.47	20.74
Ru3Ce	71	2.53	76.02	21.45
Ru5Ce	64	4.15	74.65	21.2
RuO_2	45	–	–	–