Preparation of an Electrically Heated Wire Catalyst for Cold-Start-Exhaust

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Three way catalysts were dispersed over the surface of an anodized Ti wire in order to promptly eliminate hydrocarbons remained in cold-start-exhaust gas from an automobile engine. The anodized wire was heated up to 623 K or higher in 30 sec simply by loading 13 V to the ends of the wire, which resulted in abatement of 50% hydrocarbons in the cold-start-exhausts within 30 sec just after an engine ignition.

Three-way catalysts, usually equipped for gasoline engine automobiles, work well at the temperatures higher than 623 K and are heated up to this temperature in a few minutes by an exhaust gas itself. Thus, the pollutants in the exhaust gases in a first few minutes after an engine ignition (cold-start-exhausts) are not well eliminated, since the catalysts are not sufficiently heated.[1] Hydrocarbons, not burned in an engine room, are the main pollutant in the cold-start-exhausts, and more than 20% of the unburned hydrocarbons are C_2~C_4 olefins which will cause the destruction of ozone layer.[2]

The purpose of this work is to develop a catalyst system devised for the abatement of unburned hydrocarbons remained in the cold-start-exhausts. The paper consists of two parts; in the first part the preparation and characterization of anodized Ti wire catalysts will be mentioned, and in the second part an application of the wire catalysts to cold-start-exhausts including NO, propene, oxygen and water vapor will be discussed.

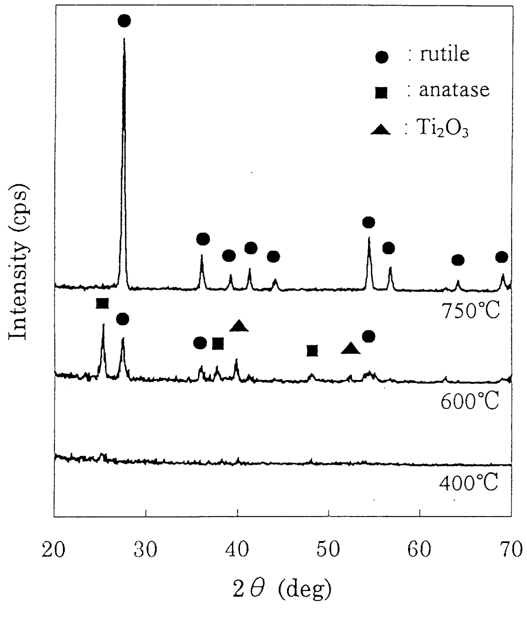

Figure 1. X-ray diffraction patterns of anodized Ti thin plate (plate was calcined at 673 K (a), 873 K (b), and 1023 K (c)).

A spiral Ti wire (1 m x 0.25 mm od, 99.5% purity) was anodized at 80 V for 30 min in a 0.16 M oxalic electrolyte at 303 K using a graphite cathode and a regulator dc supply.[3] The current observed was rapidly depressed in the first 10 sec of anodizing and then gradually decreased to a constant value (30 mA). The first depress in the current through a Ti wire means the formation of titanium oxide films over the Ti wire surface. Judging from SEM photographs (not given here) of the oxide films calcined at 873 K for 4 h, the oxide films are about 2 μ thick and less porous.

X-ray crystallographic structure of the titanium oxide films formed over the wire surface was deduced by measuring X-ray diffraction spectra of the oxide films formed on a Ti thin plate, which was anodized under the same conditions employed for the wire. X-ray spectrometer was operated at 30 kV and 15 mA using a Ni filter for CuKα radiation. X-ray diffraction patterns of the oxide films formed on Ti thin plates calcined at 673, 873 and 1023 K are shown in Figure 1. Although no diffraction peaks were detected for the oxide films calcined at 673 K, several strong peaks assigned to rutile were observed for the sample calcined at 1023 K. While for the oxide films calcined at 873 K, peaks attributed to anatase and rutile were detected because of the anatase to rutile transformation of crystal structure at 893 K.[4] Two peaks marked by a solid triangle in the Figure could be assigned to Ti_2O_3 by comparison with the pattern given in files for X-ray powder diffraction.[5] Consequently, crystallo-graphic structures of the oxide films formed over the Ti wire were determined to be the mixture of anatase, rutile and Ti_2O_3 when the anodized wire was calcined at 873 K.

The anodized wires calcined at 873 K were immersed with a suspension of fibrillar boehmite sols, prepared by hydrolysis

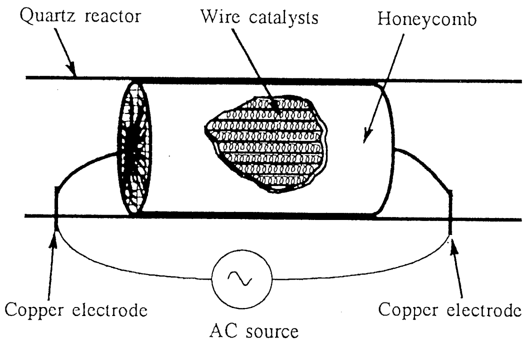

Figure 2. Wire catalysts inserted into each cell of a ceramic honeycomb.

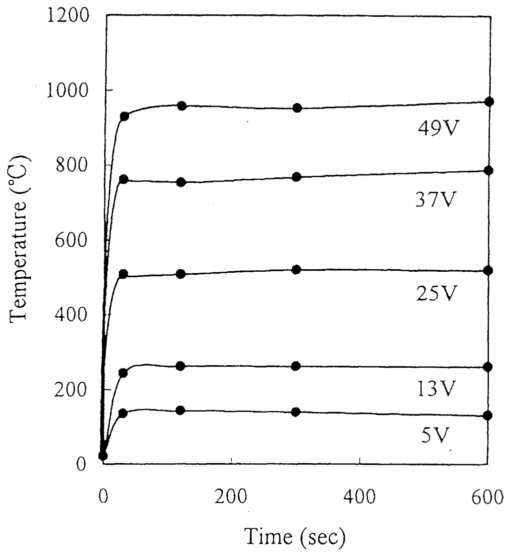

Figure 3. Relationship between temperatures and voltage charged to the ends of wires.

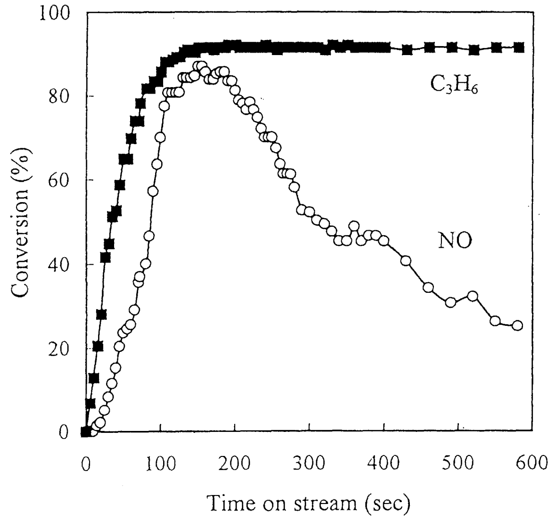

Figure 4. Rapid removal of C_3H_6 and NO by wire catalysts charged by 13 V in the presence of O_2 and water vapor.

of aluminium isopropoxide,[5] mixed with aqueous solutions of palladium, rhodium and cerium nitrates, although palladium nitrate was hard to be dissolved into water. The immersed wires were dried and calcined at 873 K for 4 h again, followed by inserting into each cell of a ceramic honeycomb, as shown in Figure 2. Amounts of Pd, Rh and CeO_2 loaded on Al_2O_3 were 0.2, 0.7 and 25.0 wt%, respectively, measured by X-ray fluorescent spectroscopy, and about 0.2 mg of the catalyst was dispersed on the surface of an anodized wire. The ends of the wires were connected with each Cu electrode equipped with a quartz reactor. The wires were promptly heated by charging a voltage to the ends of wires in flowing He, and the wire temperatures were estimated by monitoring the currents passing through wires.[6] As given in Figure 3, the temperatures rapidly reached to the constant values in 30 sec after charging .

The quartz reactor including the wire catalysts was settled in a flow system, which supplies the gases consisting of C_3H_6 (1000 ppm), NO(1000 ppm), O_2(1%) and water paper (15%), diluted by He, into the reactor with a flow rate of 10 L h^{-1}. At the outlet of the reactor, the concentrations of C_3H_6 and NO were measured by mass spectrometer and NOx analyzer. In Figure 4 are given the results obtained when 13 V was charged to the ends of wire catalysts. In the first stage of the reaction, a part of C_3H_6 were burned by the reaction with O_2 and then with NO, suggesting the difference in the light off temperatures between the reactions of C_3H_6/O_2 and C_3H_6/NO. It was found that more than 50% of C_3H_6 were burned out by charging 13 V for 30 sec, and around 70% for successive 30 sec charging. By charging 13 V for 150 sec, the conversion of C_3H_6 reached to 90% or more, hence the removal of NO began to decrease. This is the same when one will plot the conversions of both C_3H_6 and NO against the reaction temperature, instead of the charging time, for the three way powder catalyst. It should be noted that the conversion curve of C_3H_6 in the Figure was well reproduced in the absence of NO, suggesting that the reaction of C_3H_6/O_2 proceeded well without the aids by NO and NO_2.

One of the problems for electrically heated catalyst (EHC) systems is how much electricity is needed for the abatement of pollutants in automobile exhausts, since the capacity of battery equipped is usually limited to 12 or 24 V. In the present work, the current passing through wire catalysts is 21 A with a load of 13 V, then the electricity required will be around 273 W, which seems to be adequately small for practical use.

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