Rare-earth Information Center INSIGHT

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Volume 3 May 1, 1990 No. 5

Methane Conversion Catalysts

Methane is an important starting (feedstock) material for the synthesis of many products including ammonia, methanol, and higher hydrocarbons, alcohols and aldehydes. The normal route is to partially oxidize methane (CH_4) to carbon monoxide (CO) and hydrogen (H_2). The CO + H_2 product is known as synthesis gas and it is reacted with other chemicals to yield a variety of products as noted above. The current industrial process to produce synthesis gas operates at temperatures in excess of 1200°C and also produces unwanted CO_2. Scientists at the University of Oxford have discovered that rare earth-ruthenium oxides are extremely selective in only partially oxidizing CH_4 to CO and H_2 at significantly lower temperatures, ~775°C [A. T. Ashcroft et al. **Nature** 344, 319, (22 March 1990)]. The binary oxides, $R_2Ru_2O_7$ (where R = Pr, Sm, Eu, Gd, Tb, Dy, Tm, Yb and Lu), convert about 90% of the CH_4 to synthesis gas at 777°C in the presence of nitrogen gas (N_2) which acts as a diluent. All of the lanthanide elements tested were essentially equally efficient in converting the CH_4 to synthesis gas. Thus it is possible that a mixed rare earth $R_2Ru_2O_7$ catalyst would also work, however, this remains to be tested, especially since the La and Ce compounds were not examined, or at least no data were reported by the authors. In the absence of N_2 the amounts of CH_4 converted dropped significantly to about 80% on the average and there was a large variation from one lanthanide to another (e.g. 74% for $Sm_2Ru_2O_7$ to 89% for $Pr_2Ru_2O_7$). There was, however, no systematic trend in the data.

The $R_2Ru_2O_7$ catalyst has the pyrochlore structure and was prepared by direct reaction of R_2O_3 and RuO_2 powders at 1100°C. Examination of the used catalyst indicated that a partial reduction of the $R_2Ru_2O_7$ pyrochlore had occurred leading to the formation of metallic Ru on the catalyst surface. These results suggest that the active catalyst may be supported Ru metal. Indeed when a 1% Ru/Al_2O_3 supported catalyst was used under the same conditions, ~ 90% of the CH_4 was converted to CO + H_2. Although the rare earths were used to demonstrate this new and efficient methane conversion catalyst, they may not end up in the final product that is used commercially for this purpose.

Electroluminescent Displays

A potential market for high purity rare earths (~99.999% pure) is in thin film electroluminescent (TFEL) display panels. In this application the emission of colored light from the phosphor is excited by an electric field

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rather than by electron radiation as in a CRT. A TFEL cell consists of a rare earth containing phosphor layer about 1 μm thick which is sandwiched between two insulating layers (0.5 μm thick), usually made of Ta_2O_5 (but could be Y_2O_3 or Sm_2O_3). The two electrodes, which are used to apply the electric field, are made of Al (the rear electrode) and indium tin oxide (a transparent electrode). The entire cell is covered by a glass substrate. In some cases when the phosphor layer could be oxidized by the Ta_2O_5 insulating layer (i.e. SrS host doped with rare earths), a buffer layer of ZnS (0.2 μm thick) is inserted between the two layers.

Some of the phosphors being studied for use in TFEL displays are: ZnS:Tm,F - blue, SrS:Ce - blue-green, ZnS:Tb - green, ZnS:Sm,F - blue, Y_2O_2S:Eu - red, CaS:Eu - red, SrS:Ce,Eu - white and SrS:Pr,K - white. White light or broad band electroluminescence can also be realized by stacking two different phosphors, such as SrS:Ce/CaS:Eu (see below) or SrS:Ce,Cl/ZnS:Mn.

The main advantage of TFEL displays is their high resolution with none of the viewing angle problems associated with liquid crystal displays. Currently only the orange color ZnS:Mn TFEL panel is commercially available because the other colors are still too dim for utilization in panels. This problem, however, is rapidly being overcome by co-doping with other elements to improve the emission characteristics of the activator ion(s). For example, the green emitting ZnS:Tb was significantly improved by fabricating a ZnS:TbOF TFEL panel [K. Okamoto, et al., **Jpn. J. Appl. Phys. 28**, 1378 (1989)].

In addition to working on improving the lumin output of the TFEL displays, a great deal of effort is being directed at producing white light or broad band electroluminescent panels. The driving force for such panels is the demand by users of display terminals for office automation equipment for emission colors that are easy on the eyes and reduce fatigue. Recently Y. Abe et al. [**Jpn. J. Appl. Phys. 28**, 1373 (1989)] and Y. A. Ono et al. [**J. Appl. Phys. 66**, 5564 (1989)] described their efforts to produce white light emitting TFEL cells. The former double doped SrS with Pr and Ce (0.1 mol % each) to produce a bright white light with suitable color coordinates and luminance. The latter found that by stacking SrS:Ce and CaS:Eu active layers, a TFEL devise with suitable electro-optical characteristics could be fabricated. At high voltages white emission was obtained regardless of the frequency, but at low voltages the white color changed to blue-green with decreasing frequency. Furthermore, by using color filters it was possible to obtain red, green and blue emissions, which makes it possible to make multicolored TFEL devices by employing color filters.

We predict that within five to ten years TFEL displays will be an important rare earth market.

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