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IDENTIFICATION OF THE ORIGIN OF TiO$_2$ DEPOSITS
ON A HYDRODESULFURISATION CATALYST

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ABSTRACT

Mineral matter from an Eastern high volatile class A bituminous coal has been examined by scanning transmission electron microscopy and energy dispersive x-ray analysis to determine the presence of titanium containing minerals. Titanium oxide in the form of anatase (TiO₂) has been identified. Crystals of anatase having a similar morphology have been found deposited on Co-Mo catalyst particles used to promote liquefaction of the coal. This deposit has a poisoning effect on the catalytic capabilities of the particles. It has been suggested that the origin of the anatase is either as organically bound titanium in the coal which oxidises during the liquefaction process or as anatase crystallites within the coal which simply coalesce around the catalyst particles. The present observations indicate that the second of these two proposals is likely to be correct.
INTRODUCTION

Deactivation of catalysts used in the liquefaction and desulfurisation of coal is often attributed to the build up of carbon and/or metal deposits such as iron and titanium on the surface of the catalyst particles, and to sintering of the catalyst. In a previous paper Makovsky et al. investigated the nature of the titanium deposited on Co-Mo catalyst particles removed from a SYNTHOIL (fixed bed) reactor. Using x-ray diffraction they determined that the titanium compound deposited was very similar to the anatase form of TiO$_2$, with a slightly reduced lattice parameter along the c-axis. The crystallite size of the anatase-like material was estimated to be in the range 190-260Å. Two possible explanations for the origin of the anatase-like material were offered. They were (1) the titanium is originally organically bound in the coal, but becomes deposited as an oxide during coal liquefaction, or (2) small crystallites of the oxide exist in the coal and are concentrated on and around the catalyst during the liquefaction process. This paper describes investigations using conventional and scanning transmission electron microscopy (CTEM and STEM) combined with energy dispersive x-ray analysis (EDAX) of the minerals contained in the original coal to determine the presence or otherwise of anatase and of the morphology of the anatase crystals deposited on the catalyst particles.

EXPERIMENTAL

Samples of the same Homestead, Kentucky coal (PSOC 1082) as used in the liquefaction experiments were low temperature ashed to release the
mineral matter. Low temperature ashing in an oxygen plasma leaves the mineral matter virtually unchanged with some loss of organic sulphur and oxidation of pyrite. Table 1 shows the conventional ash analysis of the coal. The ash particles were dispersed ultrasonically in ethanol and then deposited on a carbon film supported on a copper grid. Material deposited on catalyst pellets used in the liquefaction process was crushed, low temperature ashed and dispersed on a carbon film. Electron microscopy was carried out on a Philips 400 scanning transmission electron microscope with energy dispersive x-ray analysis facilities.

RESULTS AND DISCUSSION

Figure 1 is a CTEM micrograph of the low temperature ash particles of the original coal. It shows the particles to have a range of sizes, up to ~5\(\mu\)m diameter, and a variety of morphologies. Figure 2 is a STEM micrograph and elemental x-ray distribution maps of the same area. The titanium content of the ash is very low (see Table 1) and this is confirmed by an EDAX scan of the area shown in the STEM micrograph (see Figure 3). The titanium is, however, concentrated in discrete particles. Figure 4 shows such a high titanium containing particle, having a roughly cuboidal morphology. The inset shows a diffraction pattern of the particle obtained by focused probe microdiffraction. Measurement of this and other diffraction patterns show that the titanium containing particles are anatase. Lattice parameter measurements from electron diffraction patterns are not as accurate as those from x-ray diffraction techniques and any variation in the c-parameter of the anatase as found
Table 1. Analysis of Mineral Matter of PSOC 1082 Kentucky Coal.

<table>
<thead>
<tr>
<th>Oxide % of HTA dry coal</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42.20</td>
<td>20.20</td>
<td>0.94</td>
<td>31.00</td>
<td>0.56</td>
<td>0.83</td>
<td>0.19</td>
<td>1.59</td>
<td>0.25</td>
<td>1.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element % total</th>
<th>Si</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.59</td>
<td>1.95</td>
<td>0.10</td>
<td>3.95</td>
<td>0.06</td>
<td>0.11</td>
<td>0.03</td>
<td>0.24</td>
<td>0.02</td>
<td>0.08</td>
</tr>
</tbody>
</table>
in the catalyst deposit cannot be detected.

Figure 5 shows a CTEM micrograph of the catalyst deposit material. X-ray diffraction has shown the deposit to contain calcite (CaCO₃), gypsum (CaSO₄·2H₂O), quartz (SiO₂) and pyrrhotite (FeₓS) as well as the anatase-like material. Figure 6 shows a STEM micrograph together with elemental x-ray distribution maps of the same area. The calcium x-ray distribution map was similar to that for iron. The large clusters of particles have a high proportion of titanium associated with them. The cluster to the left of the micrograph is predominantly titanium with some associated aluminium and silicon. Figure 7 is a higher magnification micrograph of this latter cluster showing the particles to have an angular morphology. An EDAX analysis of the cuboid shaped particle to the left of the cluster (arrowed) is shown in Figure 8. The analysis shows mainly titanium with some aluminium and silicon probably associated with adjacent particles. (Elements with an atomic number less than -12, e.g. oxygen, cannot be detected by this method. The copper peak originates from the copper grid used to support the carbon film.) Electron microdiffraction patterns from this and other titanium containing particles confirmed them to be anatase.

CONCLUSIONS

The observations show that the anatase-like constituent of the deposit on the Co-Mo catalyst used in the SYNTHOIL coal liquefaction process is in the form of roughly cuboidal particles of 2000-3000Å diameter. Anatase crystals having a similar size and morphology are found in low temperature ash obtained from the original coal. Thus,
the origin of at least some of the titanium oxide deposited on the catalyst particles may be ascribed to the presence of anatase crystals in the original coal, although the organic origin of some of the anatase deposit cannot be completely ruled out.

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This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division of the U. S. Department of Energy under Contract Number W-7405-ENG-48 through the Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania.
REFERENCES


FIGURE CAPTIONS

Figure 1. Transmission electron micrograph of low temperature ash particles from PSOC 1082 Kentucky coal.

Figure 2. Elemental distributions in low temperature ash particles from PSOC 1082 Kentucky coal: a) STEM micrograph, b) TiKα x-ray map, c) Al Kα x-ray map, d) Si Kα x-ray map, e) S Kα x-ray, f) Fe Kα x-ray map.

Figure 3. Energy dispersive x-ray analysis of particles shown in Figure 2.

Figure 4. Transmission electron micrograph of titanium containing particle in coal ash with focused probe microdiffraction pattern.

Figure 5. Transmission electron micrograph of particles deposited on catalyst pellets.

Figure 6. Elemental distributions in particles deposited on catalyst pellets: a) STEM micrograph, b) Ti Kα x-ray map, c) Al Kα x-ray map, d) Si Kα x-ray map, e) S Kα x-ray map, f) Fe Kα x-ray map.

Figure 7. Transmission electron micrograph of high titanium containing particles in catalyst deposit.

Figure 8. Energy dispersive x-ray analysis of the arrowed particle in Figure 7.
Figure 1. Transmission electron micrograph of low temperature ash particles from PSOC 1082 Kentucky coal.
Figure 2. Elemental distributions in low temperature ash particles from PSOC 1082 Kentucky coal: a) STEM micrograph, b) TiK\textsubscript{\alpha} x-ray map, c) AlK\textsubscript{\alpha} x-ray map, d) SiK\textsubscript{\alpha} x-ray map, e) SK\textsubscript{\alpha} x-ray, f) FeK\textsubscript{\alpha} x-ray map.
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Figure 7. Transmission electron micrograph of high titanium containing particles in catalyst deposit.
Figure 8. Energy dispersive x-ray analysis of the arrowed particle in Figure 7.
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