

应用于燃料电池的煤油超深度脱硫技术 及水蒸气改质技术的开发

燃料电池作为高节能性，环境负荷小的能源技术受到注目。燃料电池的氢气源现在主要利用天然气，甲醇，DME，轻质馏分，GTL，汽油和煤油等进行水蒸气改质开发。其中，煤油具有价格便宜，携带便利，常温下稳定性高，供给系统完善等优点。可以广泛应用于家庭，汽车，野外或者是灾害时，成为非常方便的电力供给源。但是用于燃料电池的燃料油中的硫磺含有量必须从现在的数十ppm减少到1ppm以下。为了达到这种严格的超深度脱硫，在现在既存的石油加工厂通过加氢精制脱硫的话，需要十分巨大的设备投资，实际上对于燃料电池用燃料油的脱硫处于无法对应状态。另外利用化学吸附的吸附型硫磺除去器正在开发中，但是吸附选择性低，使用了无法再生的高价吸附剂，处理能力也比较低。

1. 煤油的超深度氧化吸附脱硫

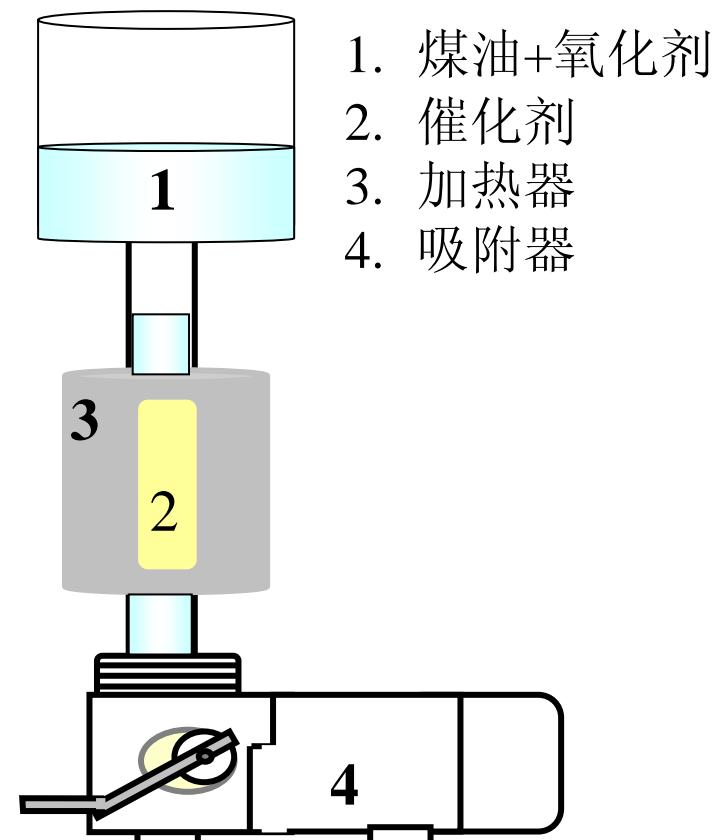
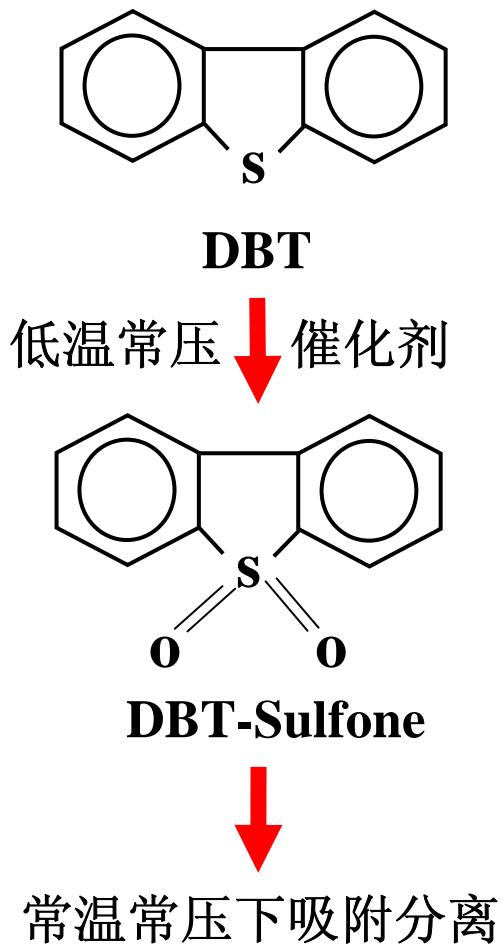
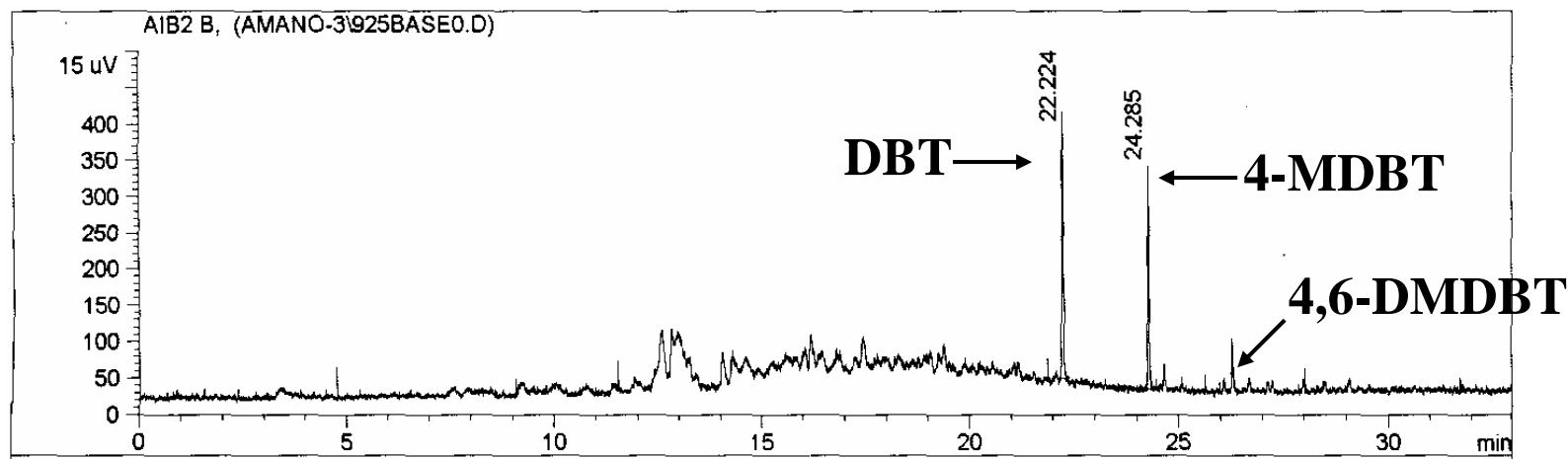


Fig. 煤油超深度脱硫器

▪ Before Oxidation



▪ After Oxidation

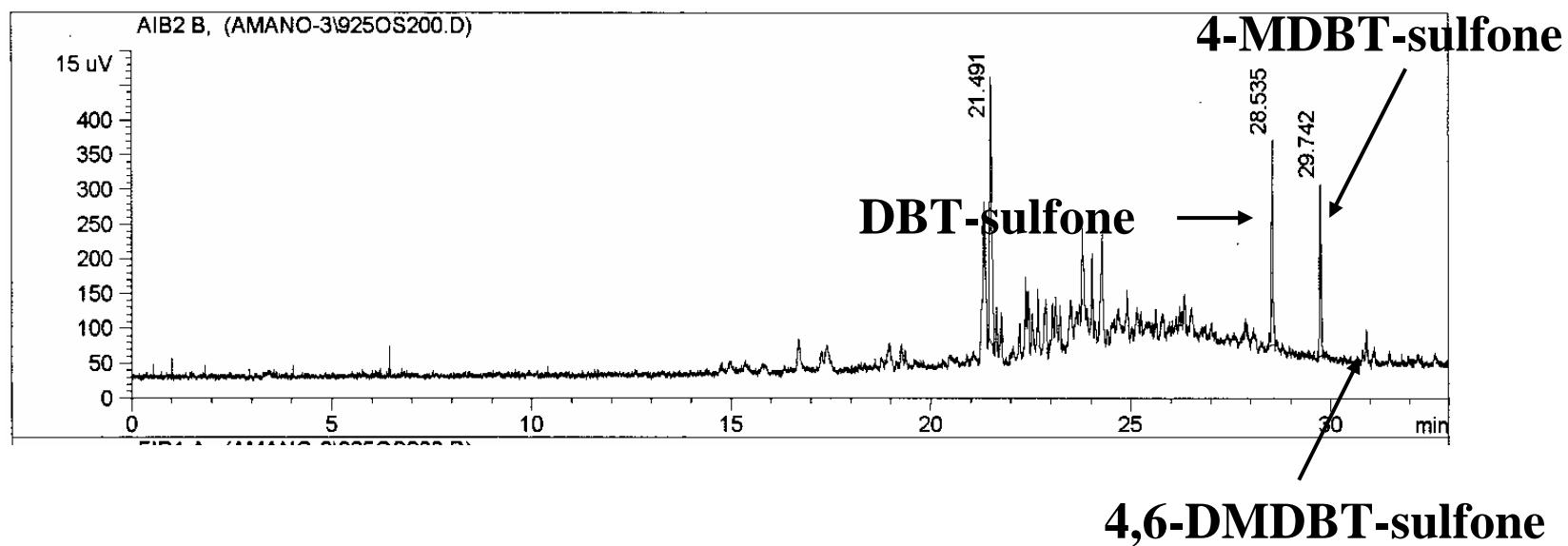


Fig. 1 SCD chromatograms of kerosene and oxidized kerosene

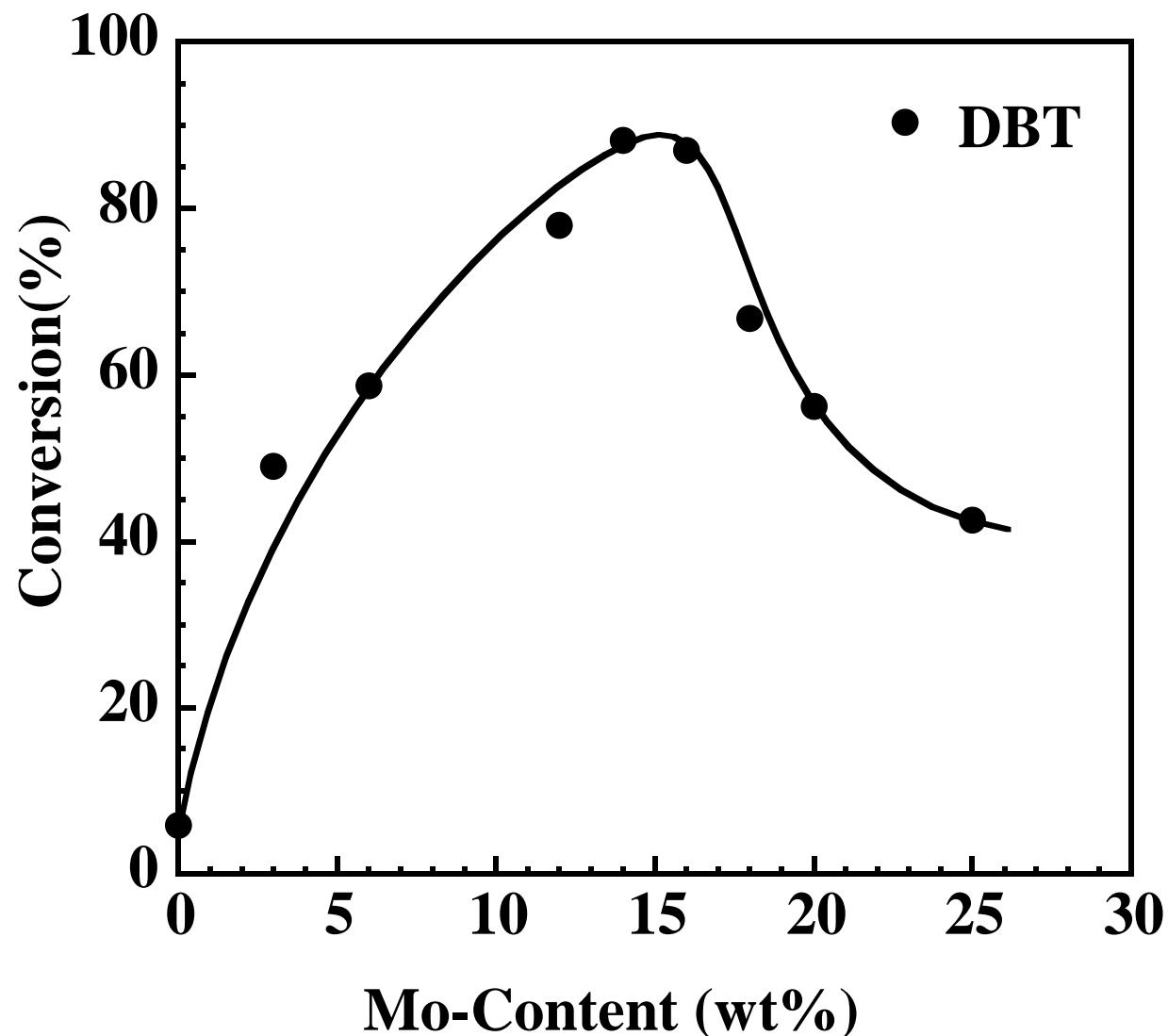


Fig. 2 Oxidation activities of DBT in kerosene on $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts with various Mo contents at 110°C

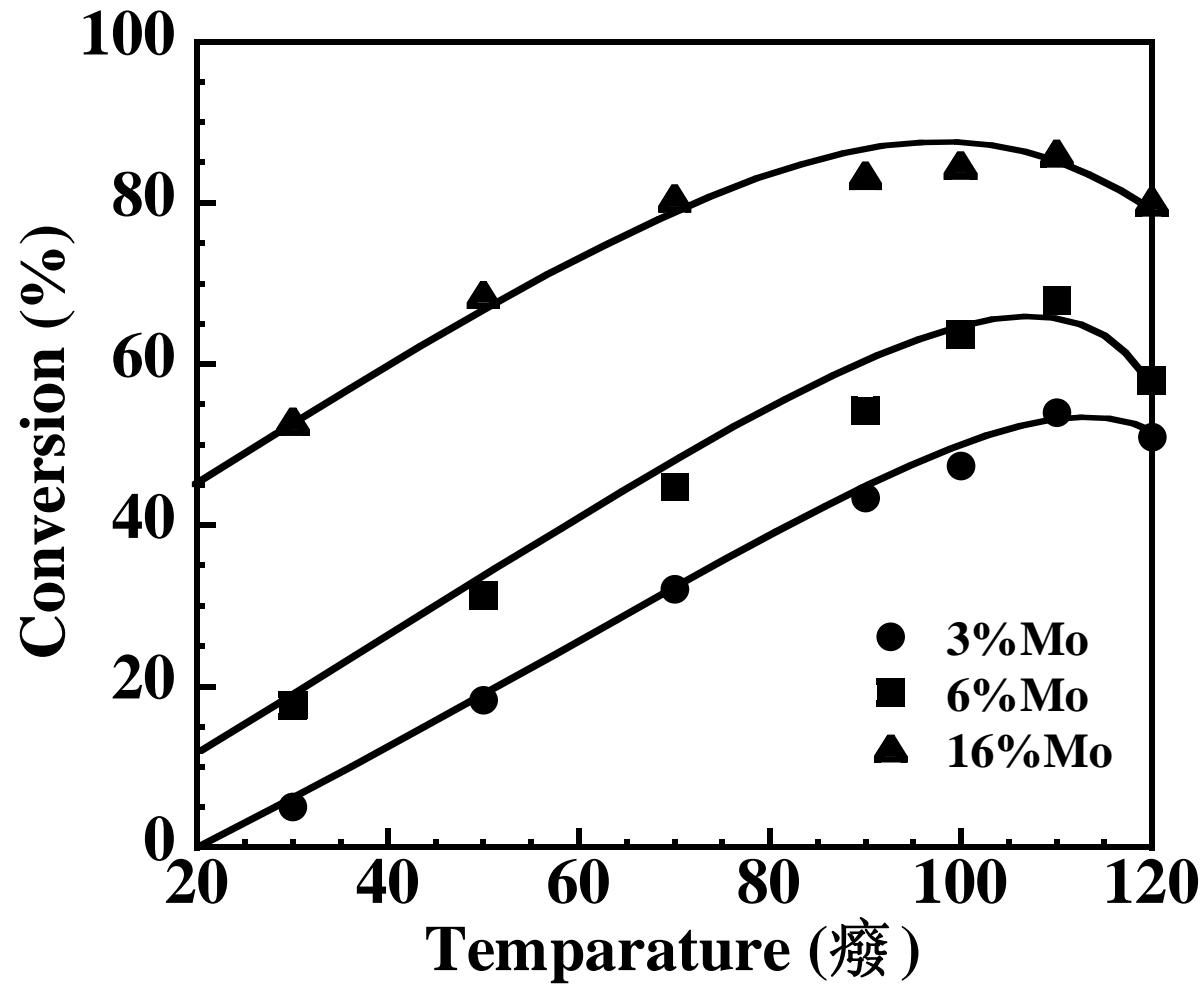


Fig. 3 Oxidation activities of DBT in kerosene on $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts at various temperatures

Table 1 Oxidation activities of DBT in kerosene on various catalysts at 110°C

| Catalyst | Conversion of DBT (%) |
|---|-----------------------|
| 16%MoO₃/Al₂O₃ | 86.13 |
| NiMo(0.4)/Al₂O₃ | 68.34 |
| CoMo(0.4)/Al₂O₃ | 23.41 |
| NiCoMo(0.4)/Al₂O₃ | 2.20 |
| 11%CrO₃/Al₂O₃ | 3.47 |
| 35%WO₃/Al₂O₃ | 78.76 |
| 10%V₂O₅/Al₂O₃ | 53.34 |
| 7%Nb₂O₅/Al₂O₃ | 43.42 |
| 15%ZrO₂/Al₂O₃ | 33.87 |
| 16%MoO₃/TiO₂ | 28.34 |
| 16%MoO₃/SiO₂-Al₂O₃ | 35.63 |

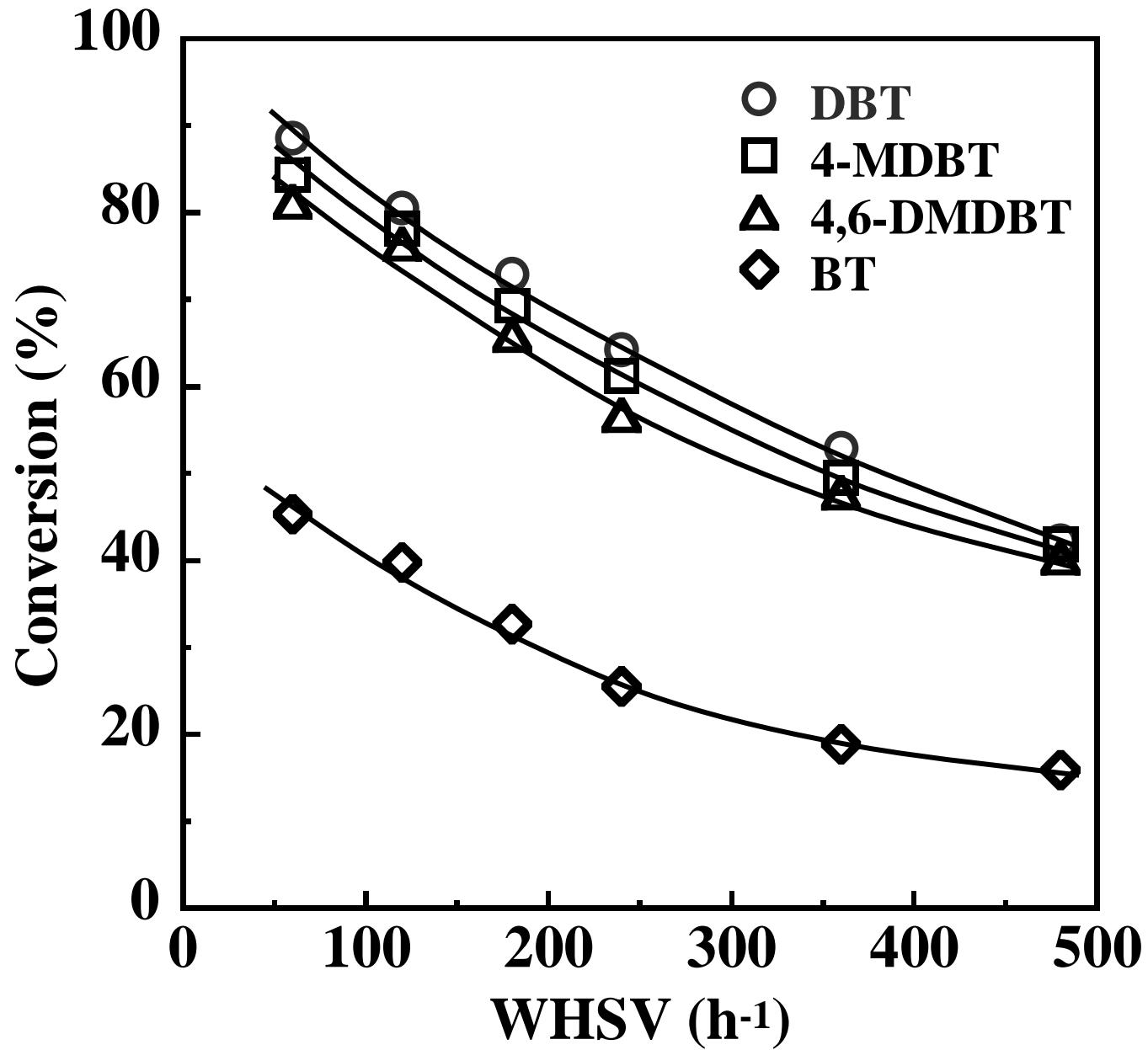


Fig. 4 Oxidation activities of model sulfur compounds on $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst under various WHSV at 80°C

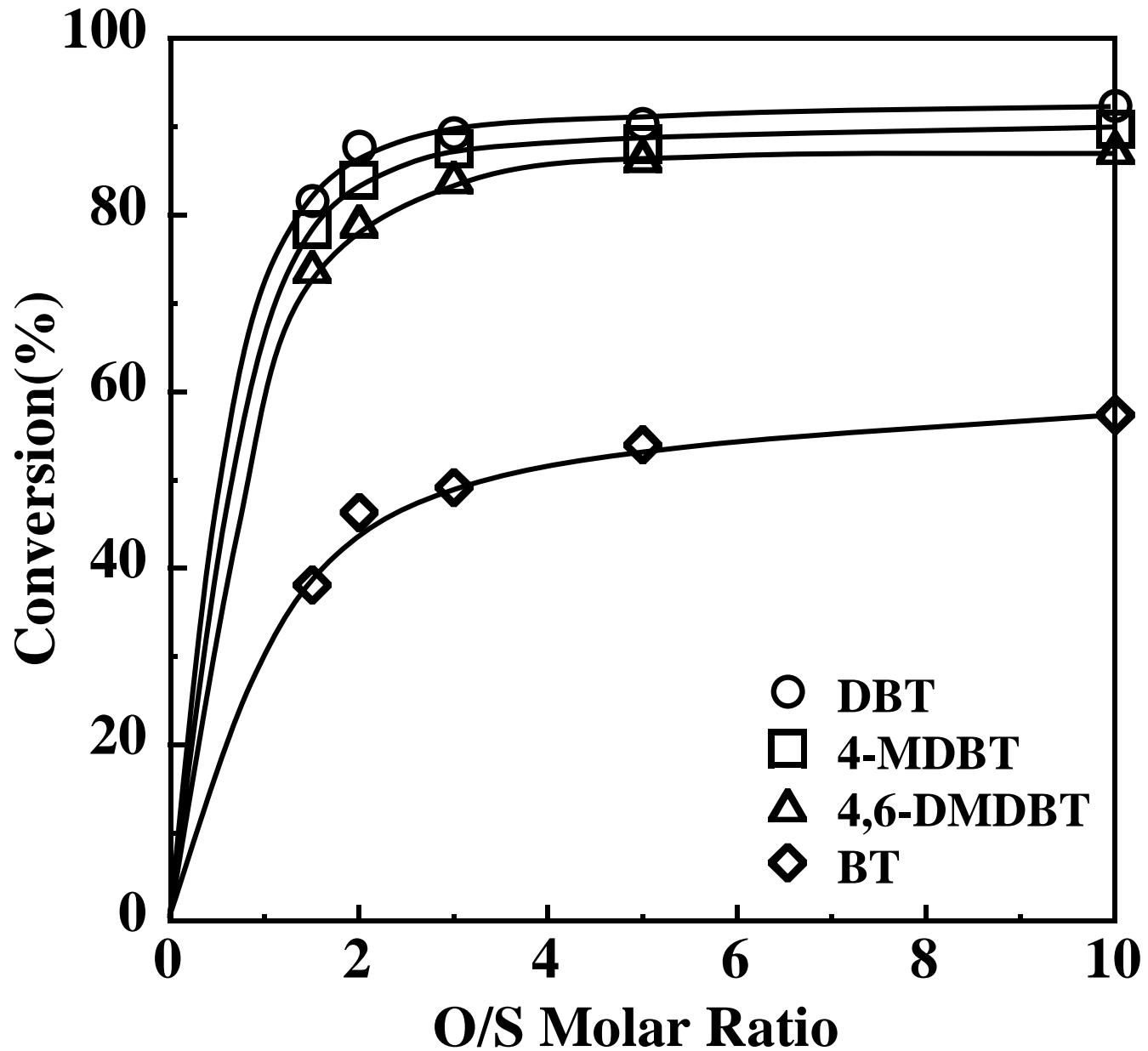


Fig. 5 Oxidation activities of model sulfur compounds on Mo/Al₂O₃ catalyst under various O/S ratios at 80°C

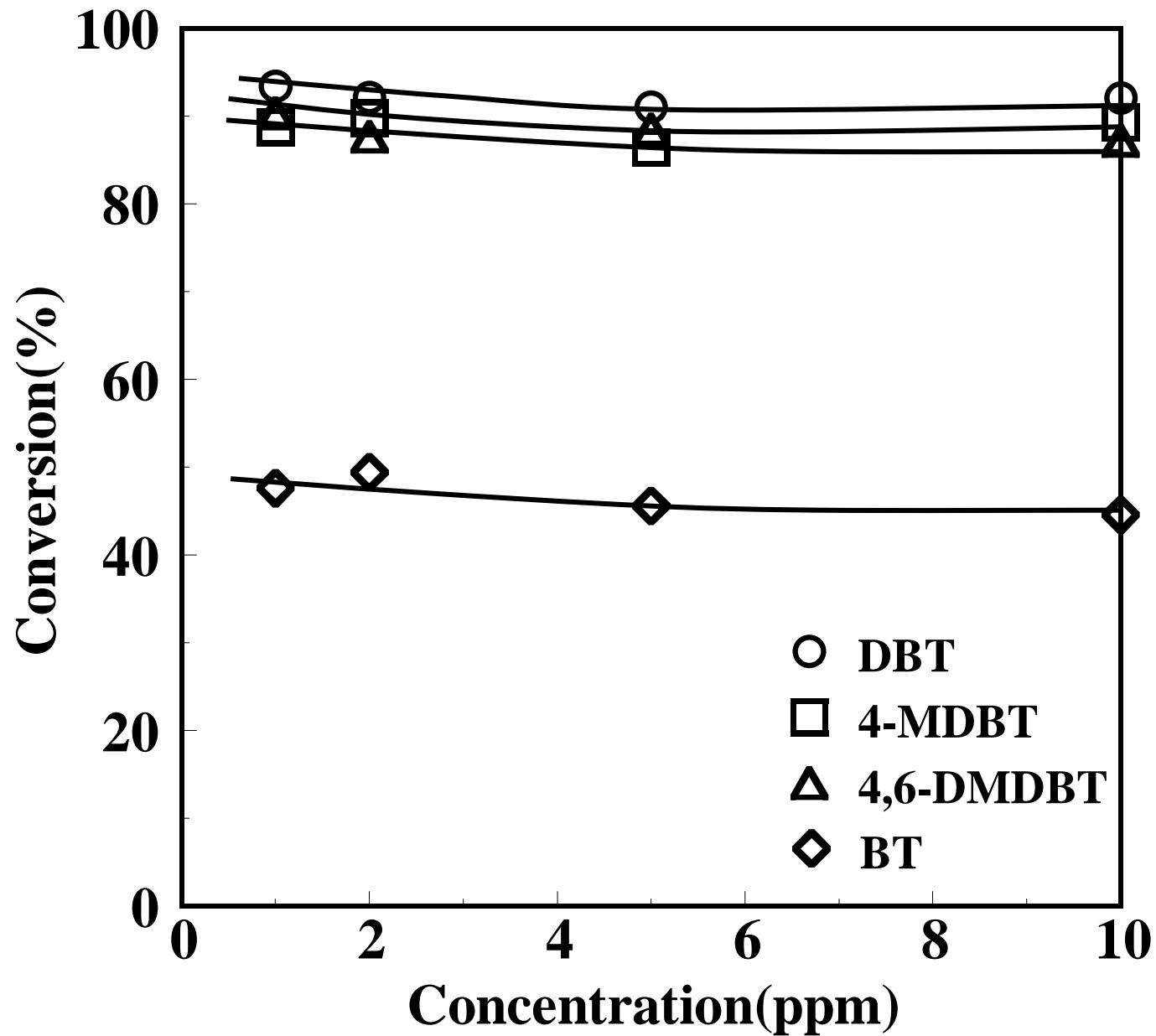


Fig. 6 Oxidation activities of model sulfur compounds on $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst under various concentrations at 80°C

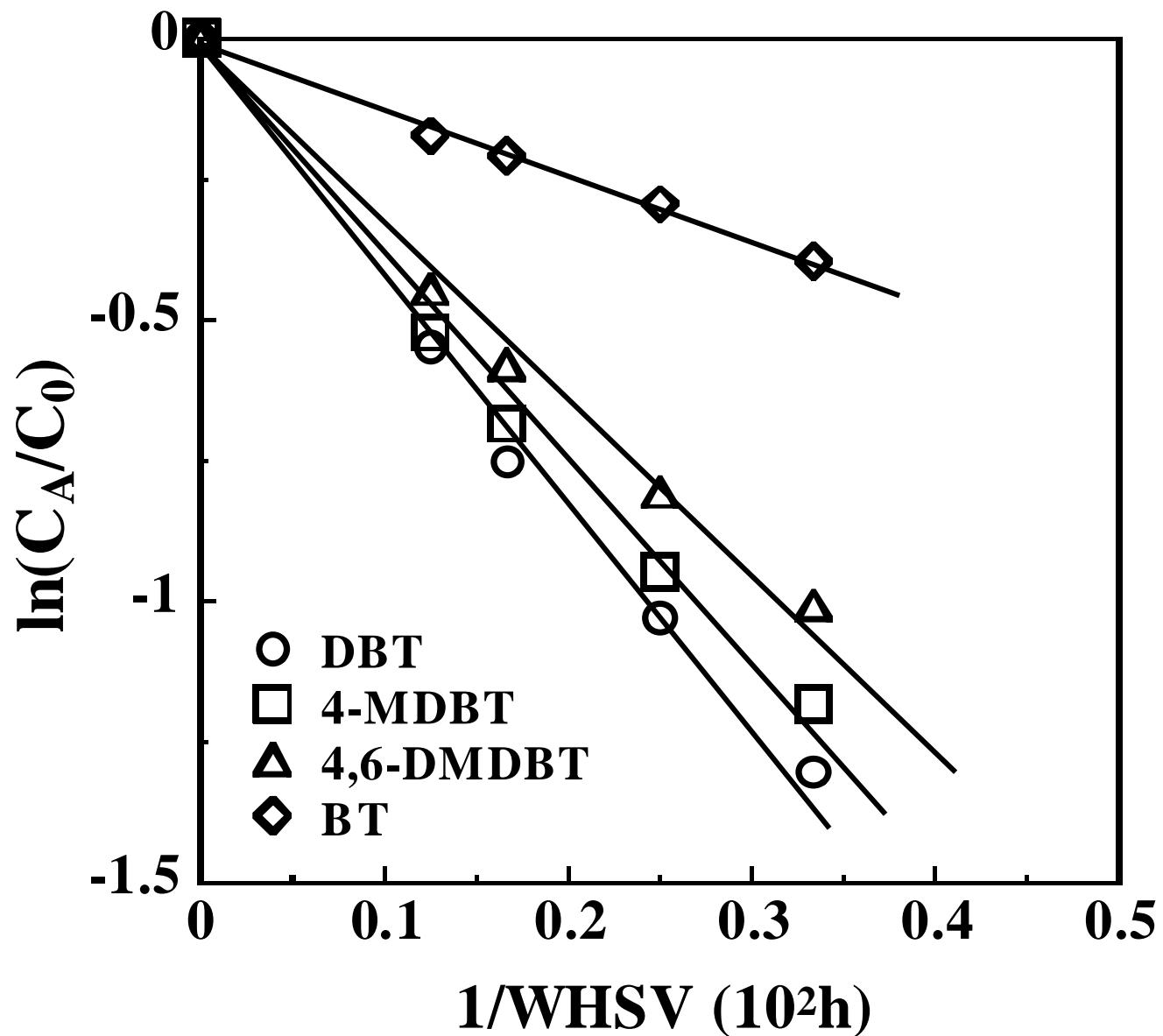


Fig. 7 The first-order plots of $\ln(C_A/C_0)$ and $1/\text{WHSV}$ for oxidation of model sulfur compounds at 80°C

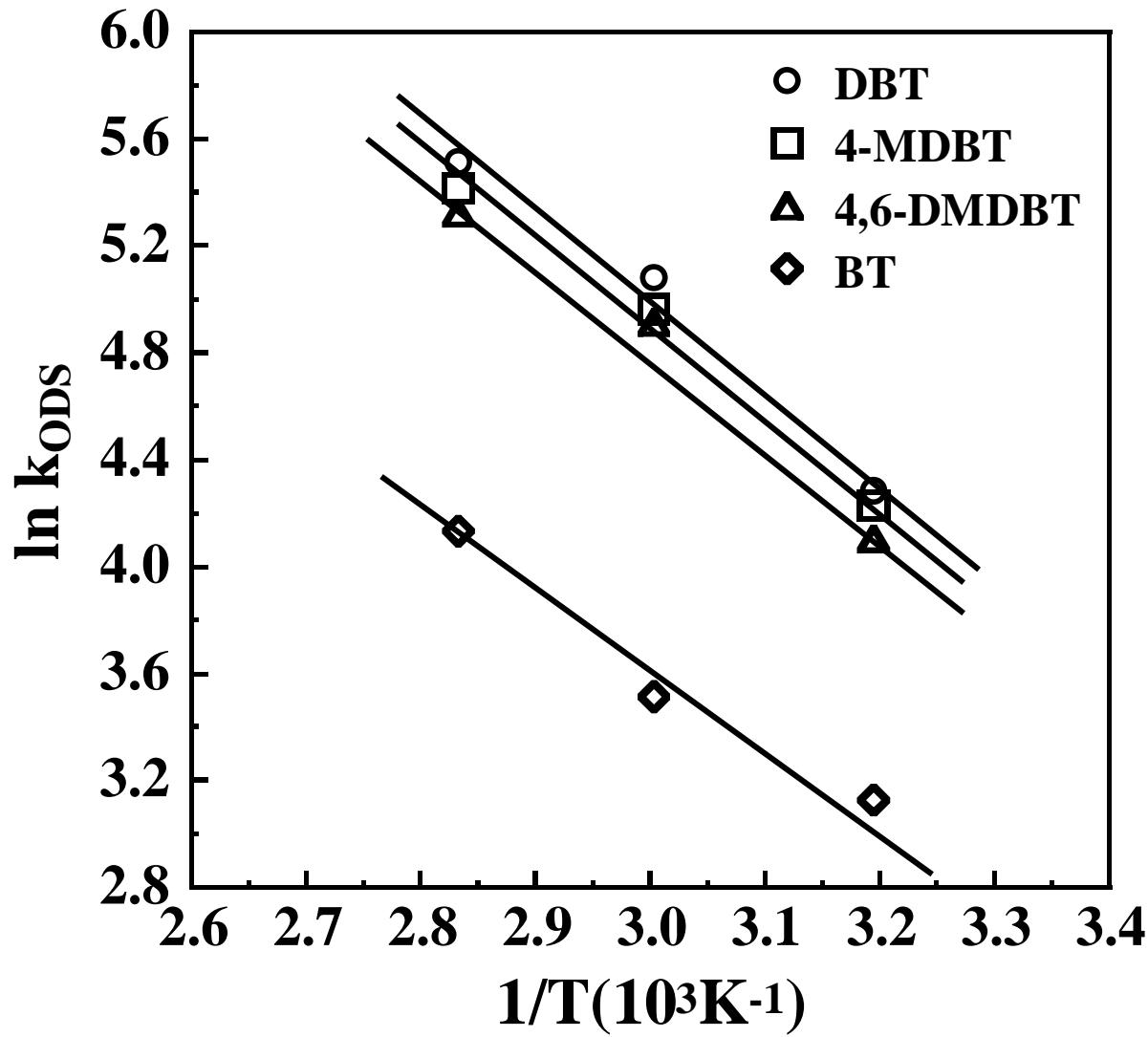
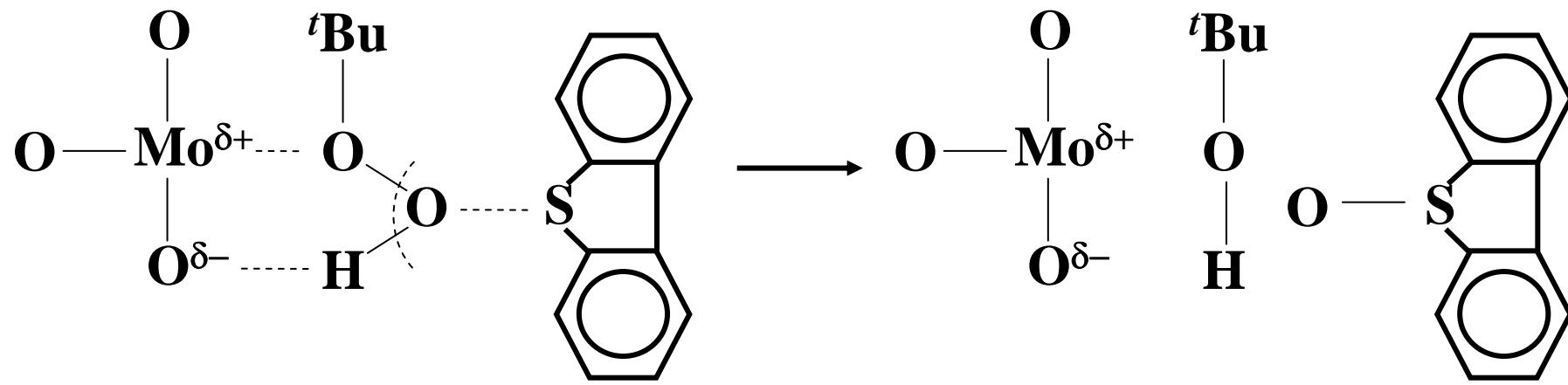


Fig. 8 The Arrehnius plots of model sulfur compounds



Scheme 1 The coordination of hydroperoxide to Mo-O on MoO_3 catalyst and peroxidic oxidation mechanism of DBT with *tert*-BuOOH

氧化吸附脱硫的结果

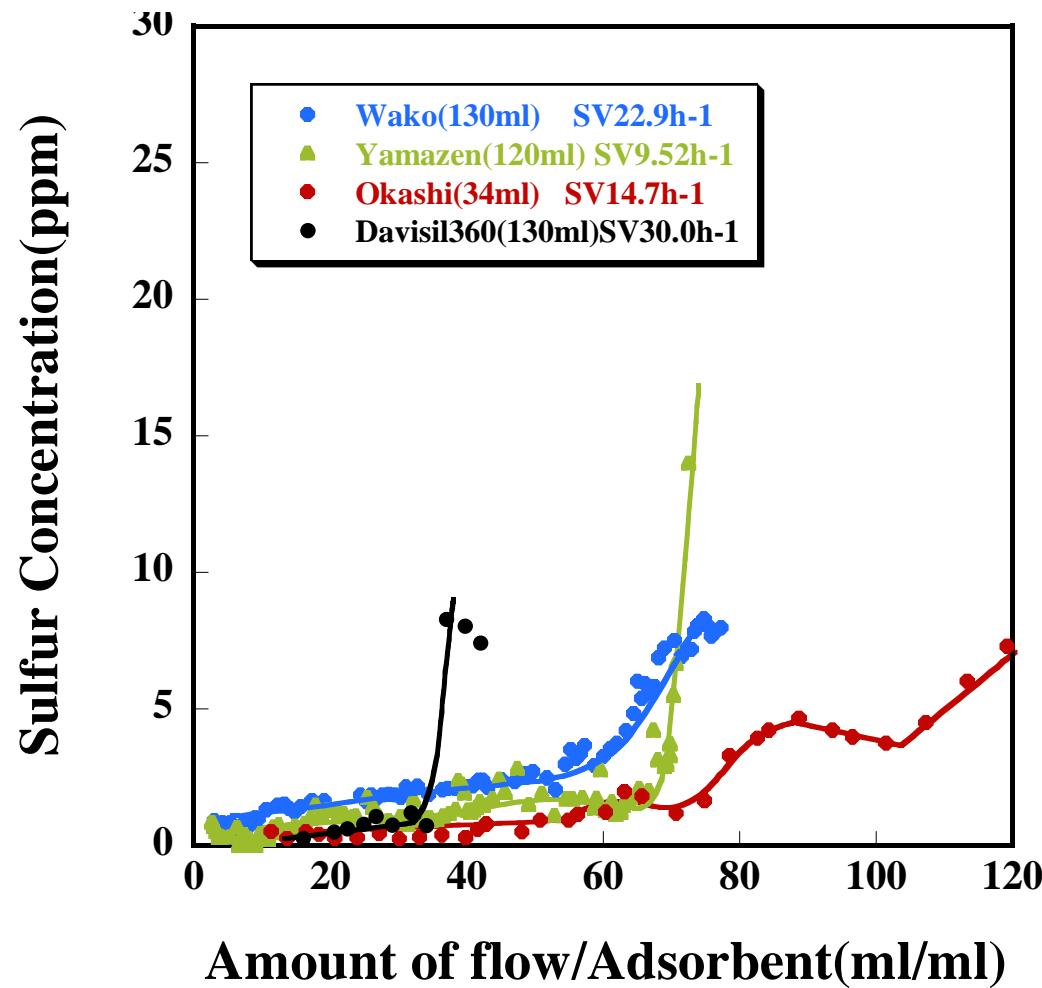


Fig. 氧化吸附脱硫结果

2. 超深度脱硫煤油的水蒸气改质反应 制备氢气

目的

用超深度脱硫煤油进行水蒸气改质反应制备氢气，开发高活性，长寿命的水蒸气改质催化剂。



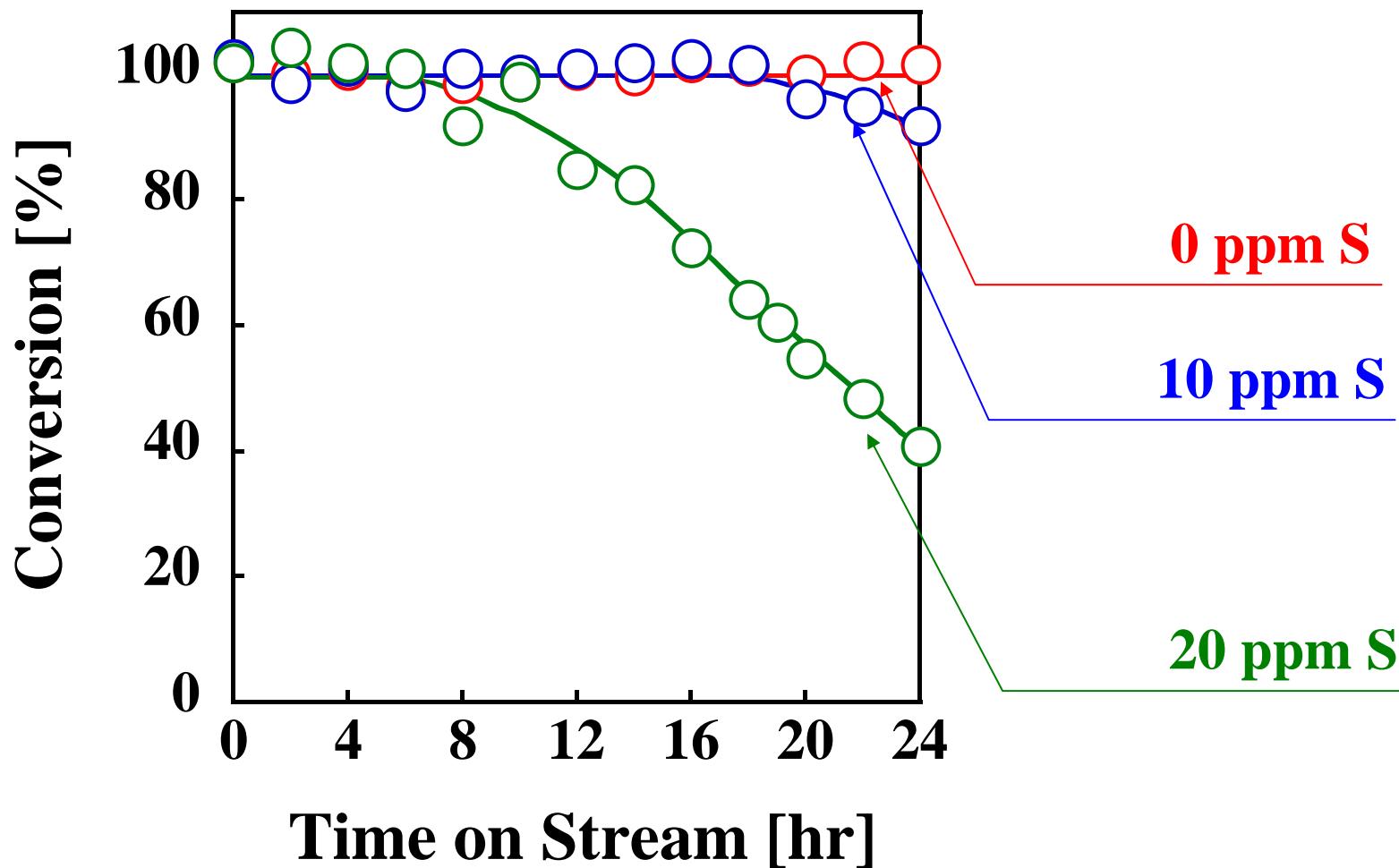


Figure 1 Effect of Sulfur concentration on GTL-kerosene conversion in steam reforming of GTL-kerosene over Ru catalyst.

(WHSV : 5h⁻¹, S/C ratio : 4, Press. : 1 bar, Temp. : 750°C)

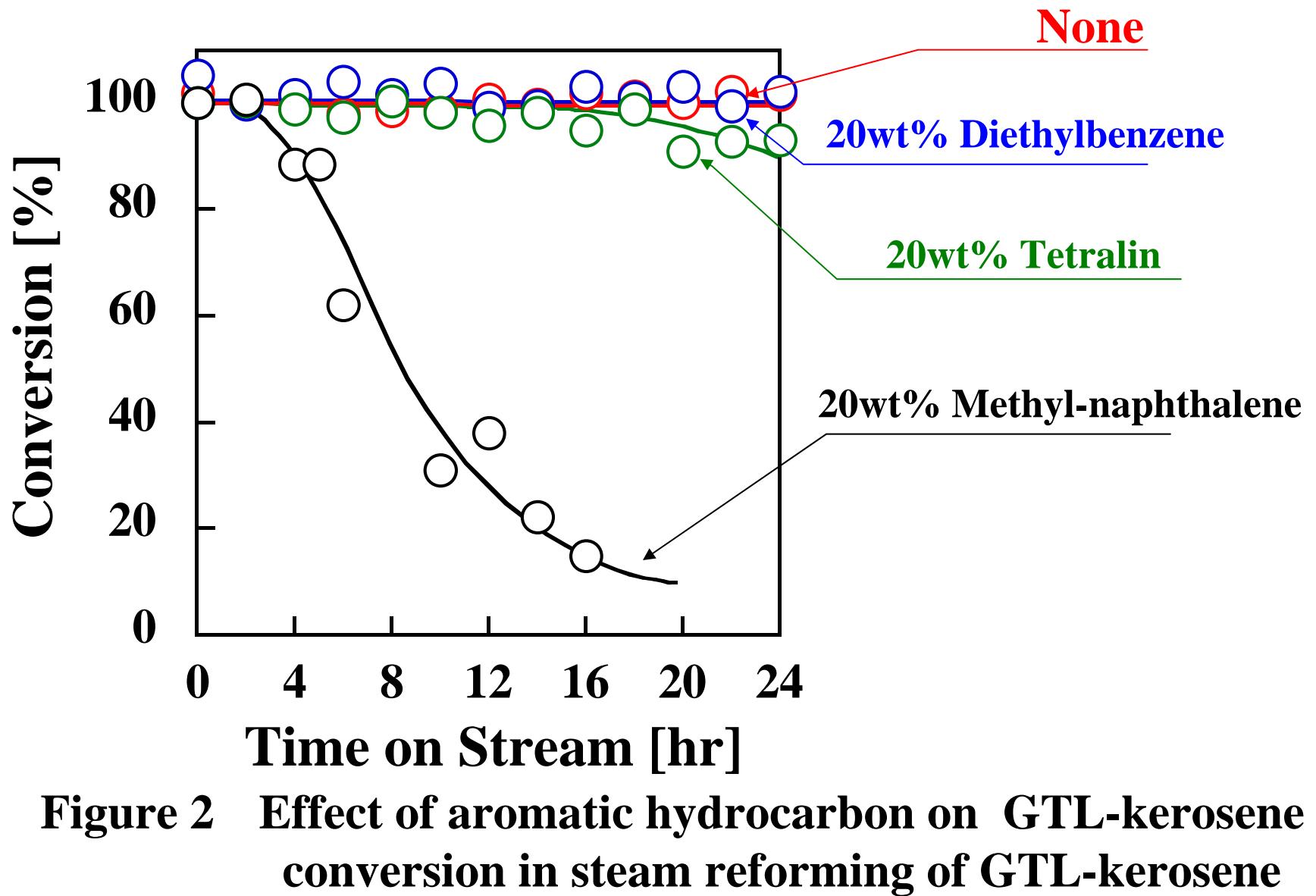


Figure 2 Effect of aromatic hydrocarbon on GTL-kerosene conversion in steam reforming of GTL-kerosene over Ru catalyst.

(WHSV : 5h⁻¹, S/C ratio : 4, Press. : 1 bar, Temp. : 750°C)

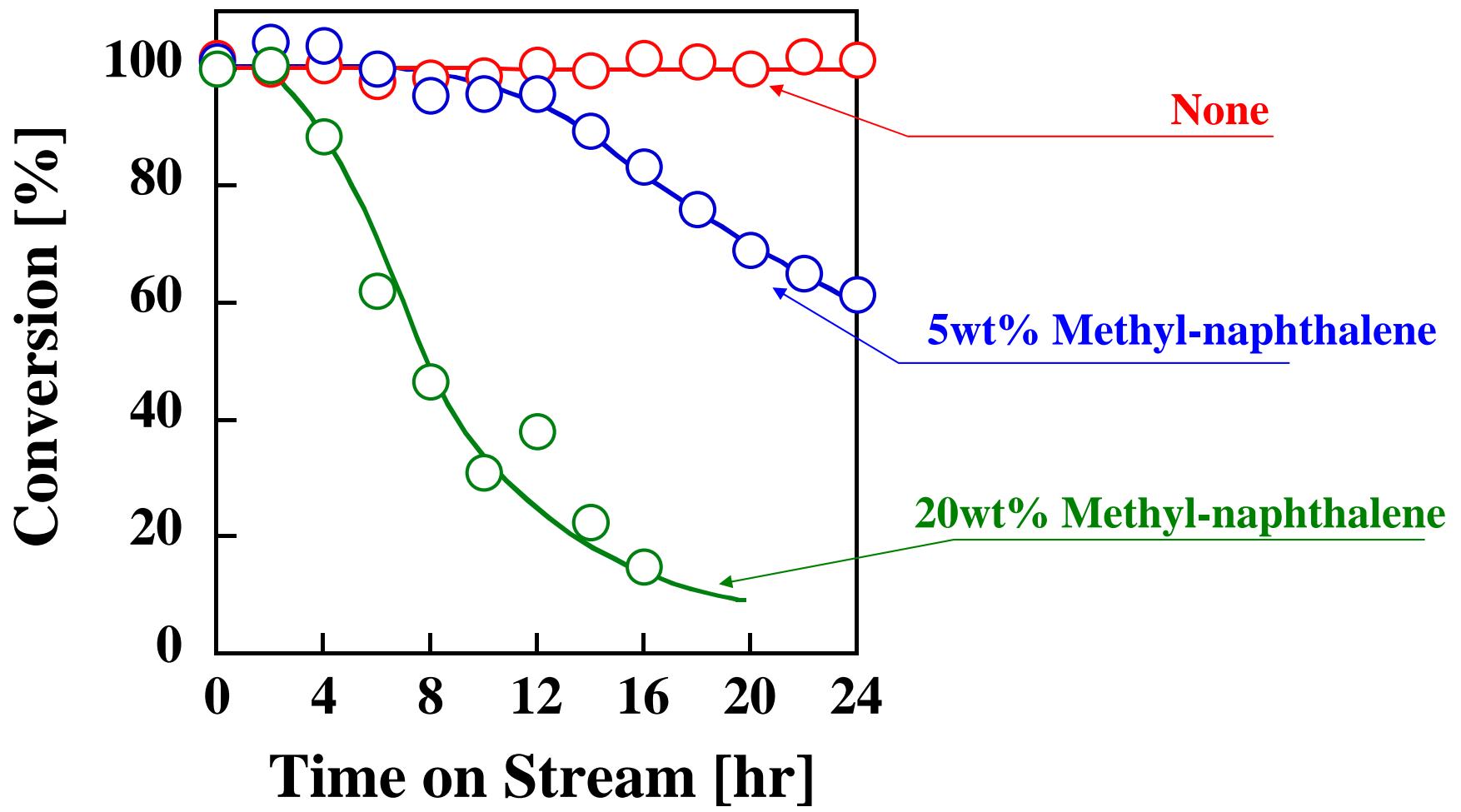


Figure 3 Effect of Methyl-naphthalene on GTL-kerosene conversion in steam reforming of GTL-kerosene over Ru catalyst.

(WHSV : 5h⁻¹, S/C ratio : 4, Press. : 1 bar, Temp. : 750°C)

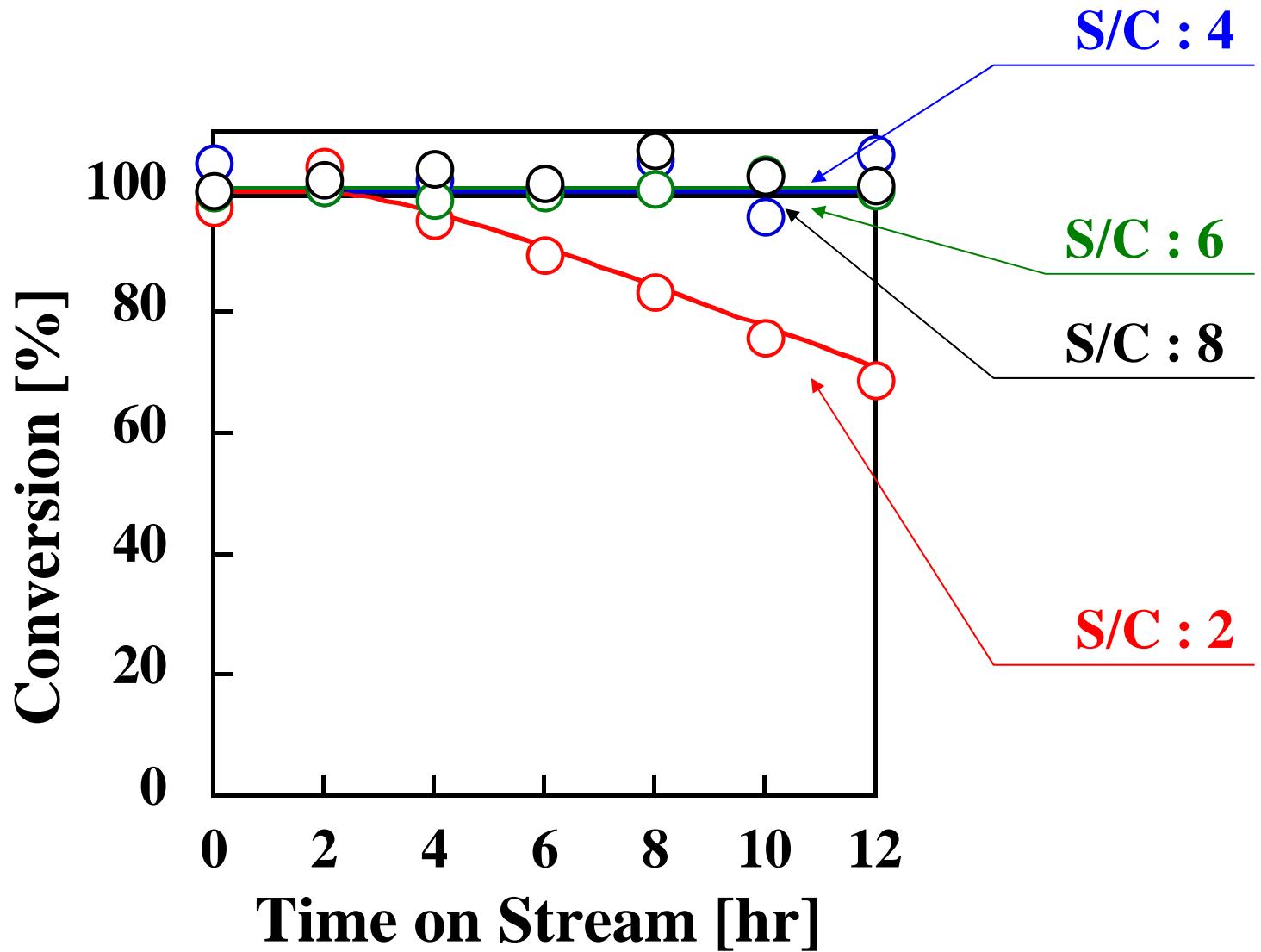


Figure 4 Effect of S/C ratio on kerosene conversion in steam reforming of kerosene over Ru catalyst.

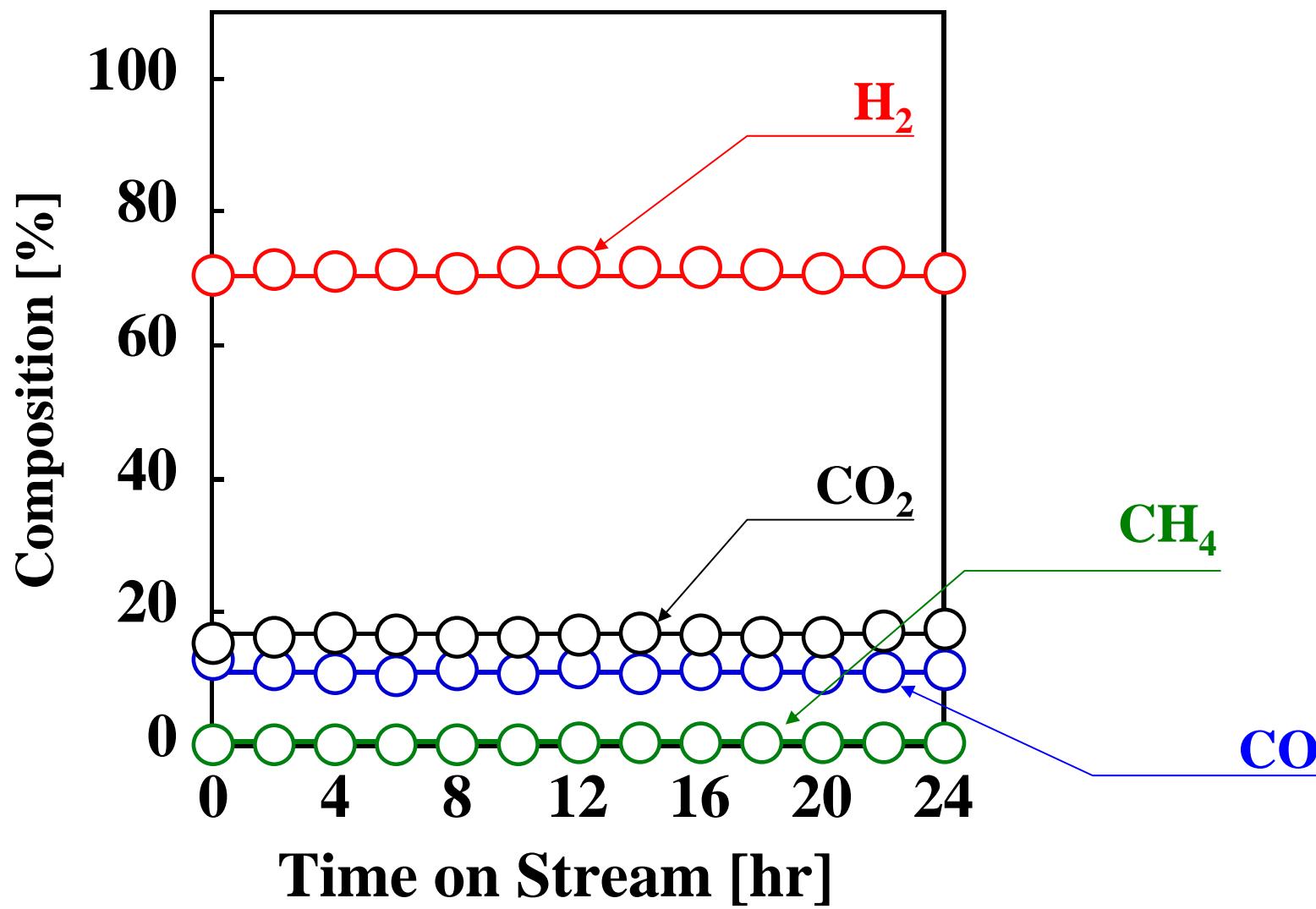
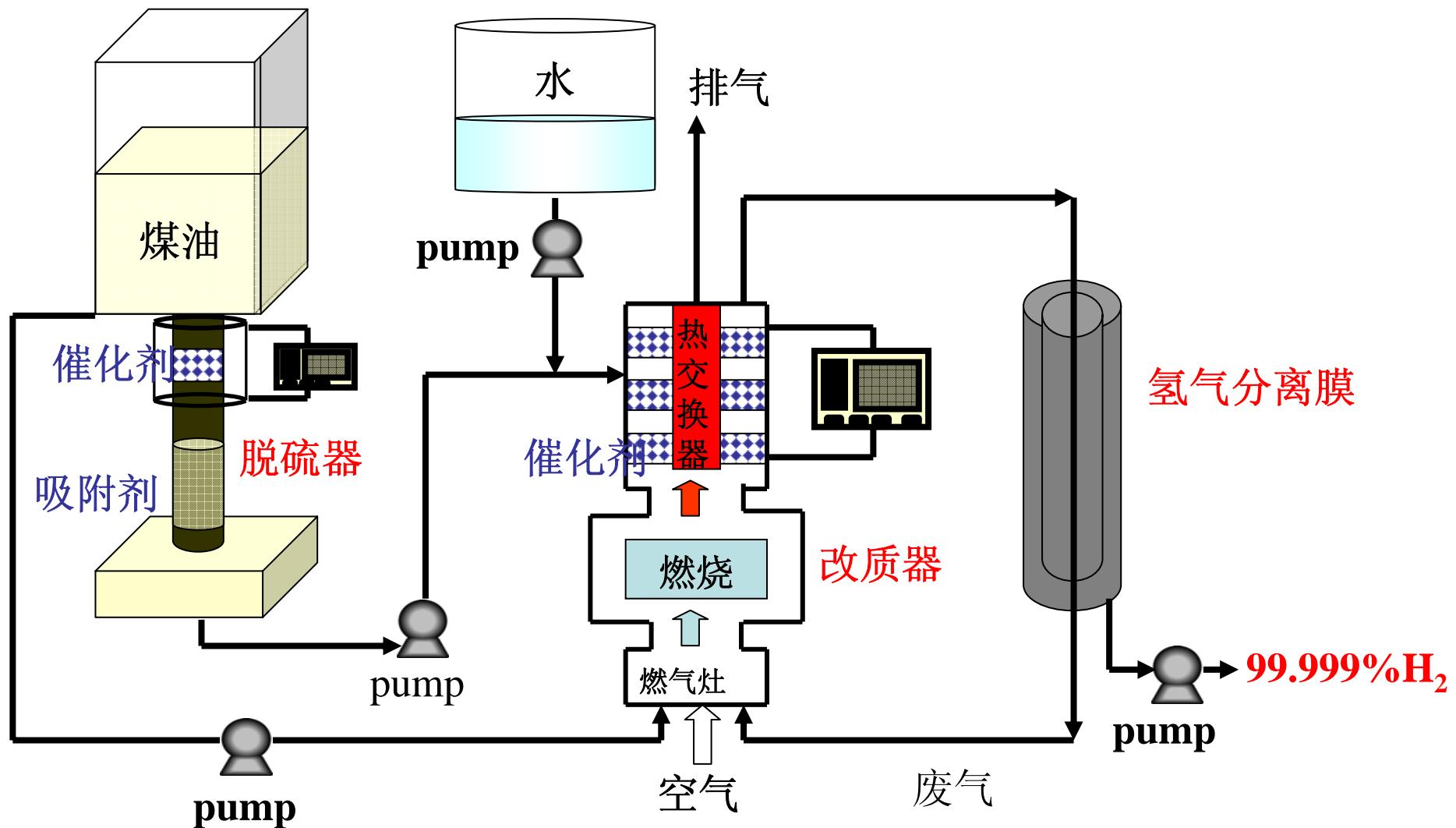


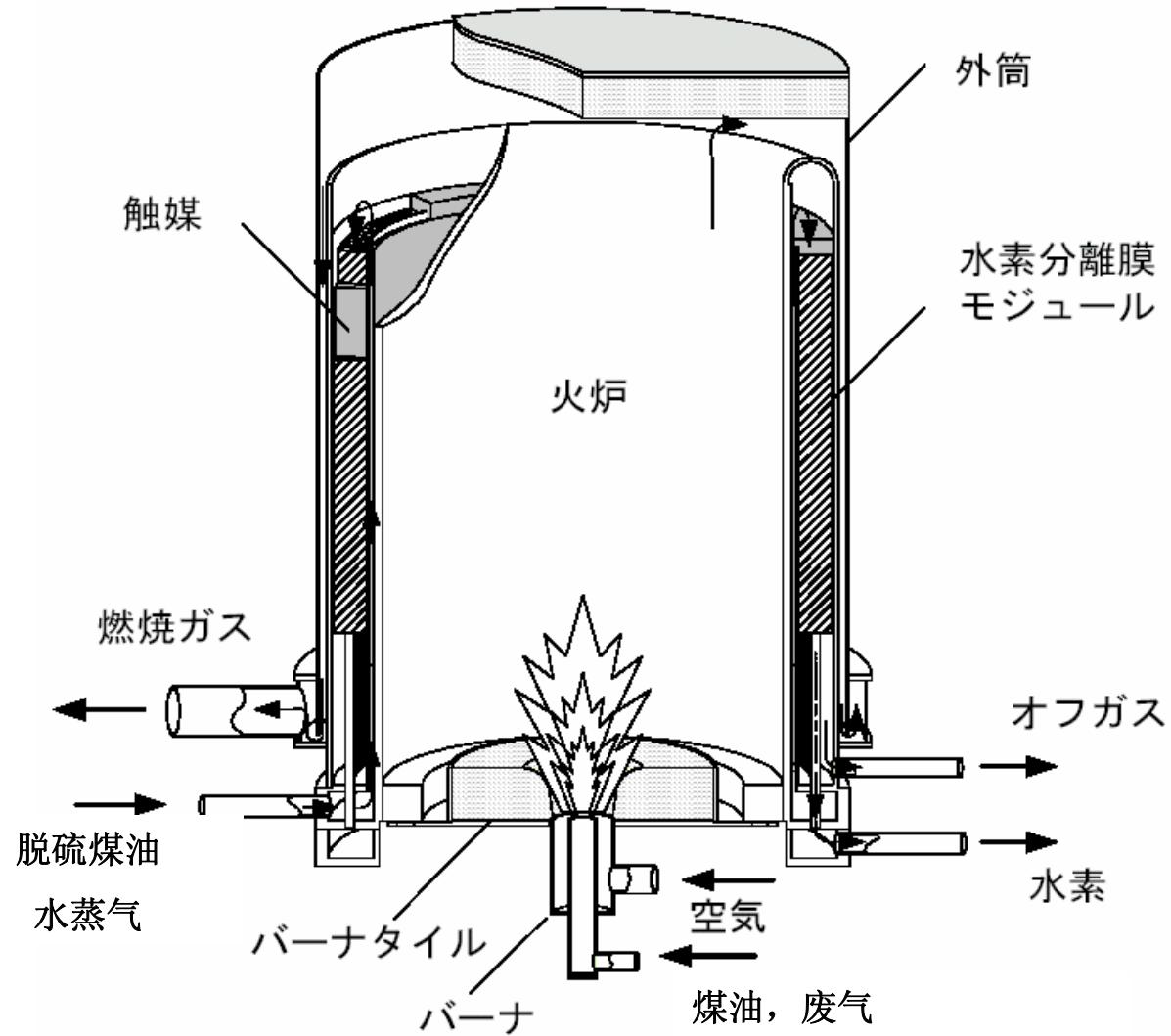
Fig.5 Changes in Product distributions in steam reforming of GTL-kerosene over Ru catalyst, at 750 °C.

3 煤油改质器的设计



实验用别体型煤油改质器的概念图

改质器的制品化设计



采用氢气分离膜的一体化煤油改质器的设计

Future Plan

- 建立一套连续的氧化吸附脱硫装置，改变催化剂，氧化条件及吸附剂，将煤油中的硫磺含量减少到0.1ppm。
- 试做一套小型化脱硫装置，进行1000, 2000, 10000小时长期试运转实验，对催化剂，吸附剂的寿命，再生的可能性，装置的长期稳定性进行考察。
- 建立一套煤油的水蒸气改质反应装置，利用超深度脱硫煤油进行水蒸气改质，开发高活性，长寿命的改质催化剂。
- 将超深度脱硫器与改质反应系统组合成试验用别体型改质器，利用煤油制造氢气提供给燃料电池。