

γ -Al₂O₃-Supported Trirhenium Clusters: Catalyst for Propylene Conversion

Rodrigo J. Lobo and B. C. Gates*

University of California, Davis, CA 95616 (USA)

*bcgates@ucdavis.edu

Introduction

Rhenium on supports is used in industrial catalysts for naphtha reforming [1] and alkene metathesis. The nature of the active sites in supported rhenium catalysts is less than well known, as a result of their nonuniformity. In attempts to prepare supported rhenium catalysts with simple, uniform structures, we used a molecular rhenium cluster as a precursor, H₃Re₃(CO)₁₂. This compound was chosen because it incorporates a framework with Re–Re bonds, which in prospect are stable enough to maintain a high dispersion of the rhenium. In this work, we have tested the catalytic properties of the supported rhenium for propylene conversion and used EXAFS spectroscopy to characterize the structure of the rhenium species.

Materials and Methods

H₃Re₃(CO)₁₂ was synthesized by a literature method [2] and adsorbed on γ -Al₂O₃ (Degusa, AluC) that had been calcined at 500°C, as before [3]. The samples were treated at 500°C in flowing H₂ for 2 h and cooled to room temperature to remove the CO ligands. In the catalytic reaction experiments, the catalyst in flowing helium was heated to 180°C, and the flow of propylene was started. The effluent gas was analyzed by on-line GC and mass spectrometry. The catalyst samples were characterized by EXAFS and IR spectroscopies.

Results and Discussion

IR spectra of the samples treated in H₂ include no bands in the region of 2200–1800 cm⁻¹, confirming the removal of CO from the metal framework. This result was confirmed by EXAFS and TPR results, the latter showing the highest-temperature peak at 450°C. EXAFS spectra characterizing the sample include a Re–Re contribution at a distance (*R*) of 2.67 Å with a coordination number (CN) of nearly 2 (1.9), which indicates that the trirhenium framework remained intact, consistent with the report of Fung et al. [3], who treated their sample at 400°C. This new result shows that the supported Re₃ clusters are stable at temperatures up to 500°C.

The data shown in Figure 1 show that the sample treated at 500°C in H₂ is catalytically active for the conversion of propylene. An induction period lasted for at least 10 h, followed by stabilization at a turnover frequency of 0.021 s⁻¹ (measured at a differential conversion <2%). The presence of ethylene and butenes in the product stream indicates the occurrence of propylene metathesis. Reactions other than metathesis also occurred, as indicated by the presence of other heavier products.

The EXAFS data characterizing a sample used for 14 h at 180°C is well represented by a Re–Re contribution at *R* = 2.64 Å, with a CN of 2.2, and a short Re–O contribution at *R* = 2.10 Å with a CN = 0.96. The data were fitted nearly as well by a different model, also including a Re–Re contribution (*R* = 2.64 Å; CN = 1.6), a short Re–O contribution (*R* = 2.07 Å; CN = 1.6), and an additional long Re–O contribution at *R* = 2.47 Å with a CN of 1.2. What is clear is that

the rhenium was present as extremely small clusters on the support and that these were stable under catalytic conditions and strongly anchored to the support. The changes in the Re–Re distance indicate structural changes in the clusters during catalysis.

Significance

Clusters derived from H₃Re₃(CO)₁₂ on the γ -Al₂O₃ surface are stable, even at high temperatures and under catalytic reaction conditions, catalyzing the conversion of propylene. Thus, the group-7 metal Re is markedly different from the group-8 metals under such conditions.

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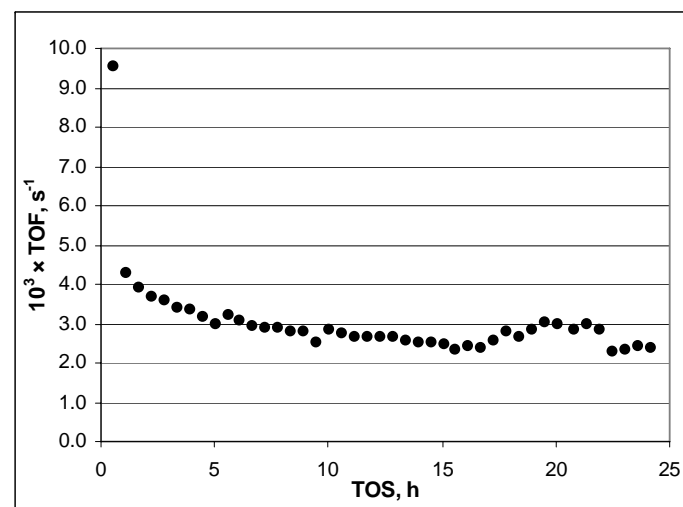


Figure 1. Conversion of propylene at 180°C with the catalyst prepared from H₃Re₃(CO)₁₂ and γ -Al₂O₃ after treatment at 500°C in H₂. The C₃H₆ flow rate was 3 ml(ntp)/min; the catalyst mass was 0.5 g.

References

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