Understanding And Eliminating Deactivation Of Rh Catalysts In Ethanol Steam Reforming

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Introduction

The Hydrogen Production Roadmap assembled by the U.S. Council for Automotive Research (USCAR), energy companies and the U.S. Department of Energy (DOE) emphasizes the potential of biomass feedstocks for hydrogen production, leading to increased energy efficiency and reduced emissions in motor vehicles and, in addition, reduced oil consumption. Distributed hydrogen production technologies, such as steam reforming of biomass feedstocks, offer one of the most viable renewable hydrogen pathways. Recent studies have identified Rh-based formulations as preferred catalysts for steam reforming of biomass-derived feedstocks with large concentrations of oxygen-containing hydrocarbons [1]. There is, however, no consensus on the causes of deactivation for Rh catalyst and on how to maintain or restore their activity. The current study evaluates the causes of deactivation of a supported Rh catalyst in steam reforming of ethanol by combining the results of catalyst testing, characterization and density functional theory (DFT) calculations.

Materials and Methods

Measurements were obtained at 650°C and a gas hourly space velocity (GHSV) of 22,000 & 44,000 h^{-1} using a flow reactor with a 300 CPSI monolith of 4 wt% $Rh/Al_2O_3/ZrO$ catalyst supplied by BASF Catalysts. The feed composition was a mixture of ethanol or E85 and steam, with the steam to carbon mole ratio of 1.8. Regeneration intervals were performed by switching from the ethanol-steam input to a flow with 50% air and 50% nitrogen, while maintaining the temperature and GHSV. Gradient-corrected DFT calculations for ethanol adsorption and reactions on Rh surfaces with a variable extent of oxidation were performed with the DMol3 code in Materials Studio software. The calculations used three surface models: (1) Rh(111) to represent Rh metal, (2) layer of $Rh_2O_3(001)$ epitaxed on top of Rh(111) to represent a partially oxidized surface and (3) $Rh_2O_3(001)$ to represent the oxide surface.

Results and Discussion

Seven cycles of reforming and pre-emptive air treatments were carried out for a total runtime of 35 h (Fig. 1). No C_2 product species were detected during the run, and complete ethanol and gasoline conversions were maintained. Using such regeneration cycles, we were able to maintain the initial catalyst activity without signs of deactivation for a test duration of 35 h. In contrast, without the pre-emptive regeneration, the catalyst exhibited deactivation in less than 14 h, and once deactivated, the initial catalyst stability could not be maintained by regeneration (not shown for brevity). XPS measurements were performed to evaluate changes in the catalyst composition with time on stream. The XPS results in Fig. 2 show that the binding energy for the Rh 3d 5/2 peak changes from 309.0 to 308.5 for fresh to pre-emptively regenerated, and then to 307.5 eV for regeneration after deactivation, indicating there is a gradual increase in the extent of Rh oxidation.

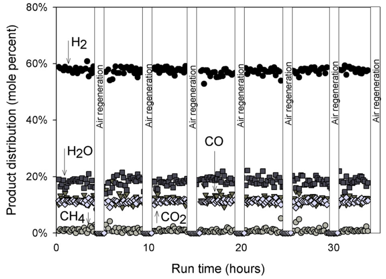

Figure 1. *Pre-emptive regeneration cycles*

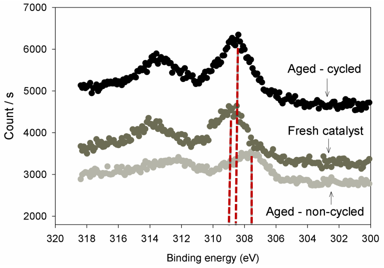

Figure 2. *XPS data showing shift in Rh oxidation*

DFT calculations show that on dissociative adsorption, ethanol splits off hydrogen from its hydroxyl group and forms CH_5O^* ethoxide and H* species shown in Fig. 3. On metallic Rh, the CH_5O^* ethoxide is predicted to be bound through the oxygen atom to a three-fold Rh site. On the partially oxidized Rh surface and on Rh_2O_3, the CH_5O^* ethoxide adsorbs on a single Rh atom as opposed to the three-fold site on the metal because there are no three-fold sites available on the oxidized surfaces: Rh atoms have only O atoms as surface neighbors. Due to this geometric difference, the preferred configuration on the oxidized surfaces is cis-gauche, as opposed to trans-gauche on the metal. In addition, the presence of lattice oxygen increases the ethanol adsorption energy significantly on Rh oxidation, from 39 to 137 kJ/mol (exothermic). Other deactivation mechanisms, such as coking, metal sintering and poisoning by impurities, were found to be less significant than changes in the extent of Rh oxidation.

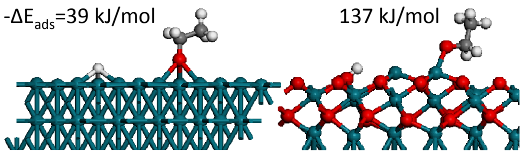

Figure 3. *Dissociatively adsorbed ethanol and adsorption energies for models representing an increased extent of oxidation: Rh metal and partially oxidized Rh.*

Our results suggest that deactivation follows a reversible mode that can be managed with air cycles and an irreversible mode developing with time on stream. Regeneration of a *deactivated* catalyst using an air flow, thus, can only partially recover the initial activity due to the long-term irreversible deactivation.

Significance

Our results show for the first time that the oxidation state of catalytic Rh nanoparticles changes dynamically under reaction conditions and the extent of Rh oxidation appears to control catalyst activity and the rate of deactivation. In addition, we identified that pre-emptive regeneration cycles with air flow can eliminate catalyst deactivation.

References

1. Bshish, A.; Yakoob, Z.; Narayanan, B.; Ramakrishnan, R., and Ebshish, A. *Chem. Pap.* 65, 251 (2011).