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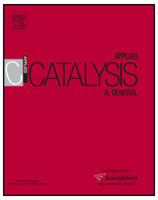

Fischer–Tropsch synthesis: Comparisons between Pt and Ag promoted Co/Al_2O_3 catalysts for reducibility, local atomic structure, catalytic activity, and oxidation–reduction (OR) cycles

Thani Jermwongratanachai[a,b], Gary Jacobs[a], Wenping Ma[a], Wilson D. Shafer[a], Muthu Kumaran Gnanamani[a], Pei Gao[a,c], Boonyarach Kitiyanan[b], Burtron H. Davis[a,*], Jennifer L.S. Klettlinger[d], Chia H. Yen[d], Donald C. Cronauer[e], A. Jeremy Kropf[e], Christopher L. Marshall[e]

[a] *Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA*
[b] *The Petroleum and Petrochemical College, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand*
[c] *Eastern Kentucky University, 4126A New Science Building, Richmond, KY 40475, USA*
[d] *NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH 44135, USA*
[e] *Argonne National Laboratory, Argonne, IL 60439, USA*

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ABSTRACT

For economic reasons, Ag as a substitute for Pt promoter for FT Co/Al_2O_3 catalysts was advocated, due to its satisfactory ability to facilitate cobalt oxide reduction, its good catalytic performance in improving the CO conversion and selectivity and, especially, its much lower price compared to that of Pt (i.e., \$23.31/Troy oz Ag. vs \$1486.0/Troy oz Pt (May 10, 2013)). A comparative study between Pt and Ag promoters at several equivalent atomic loadings was performed in this work. While either Pt or Ag significantly facilitates cobalt oxide reduction supplying additional Co metal active sites compared to the unpromoted Co/Al_2O_3 catalysts, the total metal site density increased with increasing Pt loading, but become attenuated at high Ag loading. The EXAFS results indicate isolated Pt atoms interact with cobalt clusters to form Pt–Co bonds, without evidence of Pt–Pt bond formation, even at levels as high as 5 wt% Pt. In Ag promoted Co/Al_2O_3 catalyst, not only were Ag–Co bonds observed, but Ag–Ag bonds were present, even at levels as low as 0.276% Ag. The degree of Ag–Ag coordination increased as a function of Ag loading, while decreases in BET surface area and a shift to wider average pore size suggests some pore blocking by Ag at high loadings, which likely restricted access of reactants to internal cobalt sites. Therefore, although both promoters initially facilitate reduction of cobalt oxides, their local atomic structures are fundamentally different. Either Pt or Ag can significantly improve the CO conversion rate on a per gram catalyst basis of Co/Al_2O_3. Slightly adverse effects on selectivity (i.e., increased CH_4 and CO_2, at detriment to C_5+) were found with Pt, especially at higher loading, while Ag provides some benefits (i.e., slightly decreases CH_4 and CO_2, and increases C_5+) at all loadings tested in this work. Moreover, TPR and chemisorption/pulse reoxidation results show that Pt and Ag continue to be in proximity with Co following oxidation–reduction (OR) cycles to continue to facilitate reduction. Additional reaction tests are required to determine the impact of regeneration on performance.

1. Introduction

Cobalt/alumina is an effective Fischer–Tropsch synthesis (FTS) catalyst for gas-to-liquids (GTL) production from syngas with high H_2/CO ratio (~2:1). There is general agreement that reduced Co metal surface sites are active sites for Fischer–Tropsch synthesis over this catalyst. Unlike other metals typically employed in catalysis, cobalt on alumina for FTS is often loaded in high amounts, often at or exceeding 20% by weight. Because the alumina support interacts strongly with cobalt [1,2], higher loadings facilitate the reduction of cobalt oxide species during activation and make the catalyst more resistant to deactivation (e.g., by oxidation at high conversion) [1,2]. Despite high Co metal loadings, the support still hinders the ability of cobalt oxide to be reduced during thermal activation in H_2 at moderate temperature (e.g., 350 °C for 10 h in H_2).

The addition of noble metal promoters (e.g., Pt, Ru, and Re) [2–12] significantly enhances the reducibility of cobalt oxide interacting with the alumina support and, consequently, provides

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* Corresponding author. Tel.: +1 859 257 0251; fax: +1 859 257 0302.
E-mail addresses: burtron.davis@uky.edu, leslie.hughes@uky.edu (B.H. Davis).

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additional Co metal sites for the reaction in comparison with the unpromoted catalyst. A H_2 dissociation and spillover mechanism [7,8,13] is believed to be a possible way of promotion, in which the promoter metal, first reduced at lower temperature such that H_2 dissociates and spills over from the metal promoter to form nuclei of Co^0 in the cobalt oxide, with this reduced cobalt expediting further reduction of cobalt oxide particles. Among these noble metal promoters, Pt promoter is among the most widely used in commercial FT Co/Al_2O_3 catalysts. PtO_2 has been observed after calcination [14], while only a Pt–Co bimetallic phase was found in the $Pt–Co/Al_2O_3$ catalyst [7,15,16] after activation in H_2, as investigated by EXAFS spectroscopy. This structural coordination was suggested to be responsible for facilitating Co reduction and thereby improving the CO conversion rate on a per gram catalyst basis.

Group 11 metals (Cu, Ag, Au) have been investigated as potential substitutes for Pt [13], due to their ability to facilitate reduction of cobalt oxides and, in particular, due to the lower prices of Ag and Cu compared to that of noble metals like Pt. We found that although all the Group 11 metals enhanced the reducibility of cobalt oxides and increased the fraction of Co reduced, there were differences in catalytic activity and selectivity: introducing Ag or Au (the latter at lower levels) improved CO conversion and slightly improved reaction selectivity relative to the unpromoted catalyst, while adding Cu, the catalytic activity and selectivity were worse than those of the unpromoted catalyst. Because of the good performance of Ag in facilitating cobalt reduction and in performance together with its lower price compared with Au, Ag appears to be the best among Group 11 metals and to be the most promising promoter as a substitute for Pt, a promoter used commercially. Well dispersed Ag_2O was suggested to be the main Ag species in a $Ag–Co/Al_2O_3$ catalyst after calcination or oxidation [13,17] and this species quickly reduced during activation conditions [18]. In our preliminary study of the local atomic structure of $Ag–Co/Al_2O_3$ catalyst Ag–Co coordination was difficult to assess due to the high loading of Ag used [13]. Notwithstanding, because of the ability of Ag to facilitate Co reduction and to slightly reduce CH_4 formation as observed in our recent work [13], Ag–Co coordination is expected to be detected at lower Ag loadings, and this was investigated in this work using the EXAFS technique and measuring at the Ag K-edge. Adding Ag to hydrogenating catalysts can hinder the hydrogenation reaction and Ag-active metal bimetallic was proposed to be an active site [19]. This could shed light on why CH_4 selectivity is decreased in the Ag promoted Co FT catalyst.

A comparative study between Pt and Ag was conducted in this work. Although proposed in our previous report on the role of Pt [7] and Ag [13] promoter, one objective of this work was to determine if higher loading could further facilitate cobalt reduction, and subsequently find the point at which Pt–Pt bonds could be identified in the case of Pt promotion or the point at which Ag–Co could be found in the case of Ag, which were not disclosed before; moreover, the most appropriate Pt and Ag loading will be suggested. In so doing, different levels of atomically equivalent loadings of Pt or Ag were applied to $25\%Co/Al_2O_3$. Standard characterization methods (e.g., H_2 TPR, H_2 chemisorption/oxygen pulse reoxidation, X-ray diffraction, and BET) were also employed. The catalysts were thoroughly characterized at the atomic level by EXAFS spectroscopy, while electronic information was also obtained by XANES. Moreover, CSTR tests were implemented at ~50% conversion level so that FTS selectivities could be directly compared between Pt and Ag promoted cobalt catalysts. The final investigation in this work was a preliminary investigation of the potential of catalysts to be regenerated, and this was carried out using oxidation–reduction cycles. However, additional studies are needed in this area.

2. Experimental

2.1. Catalyst preparation

The catalyst support used was Sasol Catalox-150 $\gamma-Al_2O_3$. To achieve 25%Co loading, a slurry impregnation method, which follows a Sasol patent [1], was used. Cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$) (Alfa Aesar) was employed to make the Co precursor solution. The ratio of the volume of loading solution used to the weight of alumina was 1:1, such that approximately 2.5 times the pore volume of solution was used. Two impregnation steps of cobalt nitrate were applied. Between each step the catalyst was dried under vacuum in a rotary evaporator. After the last step of cobalt addition, platinum or silver precursor solution was added to the Co/Al_2O_3 catalyst by incipient wetness impregnation. Tetraamine platinum(II) nitrate solution and silver nitrate (Alfa Aesar) were utilized as Pt and Ag sources, respectively. A series of Pt promoted Co/Al_2O_3 catalysts was prepared with loadings of 0.5%, 1%, 2%, 3%, 4%, and 5%, which are atomically equivalent to Ag loadings of 0.276%, 0.553%, 1.11%, 1.66%, 2.21%, and 2.76%, respectively. Only after the final step were catalysts calcined under air flow at 350 °C for 4 h.

To study the potential of each catalyst to be regenerated, oxidation–reduction (OR) experiments mimicking catalyst regeneration cycles were performed for both Pt promoted and Ag promoted catalyst. First, the freshly calcined catalysts were reduced at 350 °C for 10 h under flow of 25% H_2 in helium, then cooled to room temperature under H_2 flow and purged with nitrogen and, subsequently, passivated by 1% O_2 in nitrogen flow at room temperature. After that, oxidation was performed at 350 °C for 4 h under flow of air. 2 cycles of oxidation–reduction (OR) experiments were done with each catalyst in this study and the catalyst samples were withdrawn after each cycle for the purpose of characterization.

2.2. BET surface area and porosity measurements

The measurements of BET surface area and porosity of the calcined catalysts were conducted using a Micromeritics Tri-Star system. Before performing the test, the temperature was gradually ramped to 160 °C and the sample was evacuated at least 12 h to approximately 50 mTorr. The BET surface area, pore volume (single point), and average pore radius (single point and BJH adsorption) were obtained for each sample.

2.3. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) profiles of calcined catalysts were recorded using a Zeton-Altamira AMI-200 unit equipped with a thermal conductivity detector (TCD). Samples were pretreated by purging with argon flow at 350 °C to remove traces of water. The TPR was performed using a $10\%H_2/Ar$ gas mixture and referenced to argon at a flow rate of $30\,cm^3/min$. The sample was heated from 50 to 800 °C using a heating ramp of 10 °C/min.

2.4. H_2 chemisorption and percentage reduction by pulse reoxidation

Hydrogen chemisorption was conducted at using temperature programmed desorption (TPD), also measured with the Zeton-Altamira AMI-200 instrument. The sample weight was typically ~0.220 g. Catalysts were activated in a flow of $10\,cm^3/min$ of H_2 mixed with $20\,cm^3/min$ of argon at 350 °C for 10 h and then cooled under flowing H_2 to 100 °C. The sample was held at 100 °C under flowing argon to remove and/or prevent adsorption of weakly bound species prior to increasing the temperature slowly to 350 °C,