Operando IR/EXAFS Studies of the Promotion-Inhibition Behavior of Pt-NbO$_2$/Al$_2$O$_3$ Catalysts during the Preferential Oxidation of CO

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Introduction

Fuel cells have the potential capacity of providing a clean and efficient source of electrical power for both mobile and stationary applications. The fuel needed by these cells is hydrogen or hydrogen-rich feed gas, which can be obtained from a methanol-reforming unit preceding the fuel cell among other sources. The H$_2$-rich exit stream from a reformer typically contains 0.5-2% carbon monoxide, CO [1, 2]. CO in the cell feed needs to be as low as 20 ppm to avoid poisoning the platinum anode. This can be achieved in a special catalytic unit preceding the fuel cell, where CO is preferentially oxidized to CO$_2$ (PROX reaction) [3]. This work reports the effect of niobia addition to Pt-based catalysts applied to the PROX reaction. An interesting promotion-inhibition behavior was observed, which depends on Nb loading.

Materials and Methods

The 1%Pt/Al$_2$O$_3$ and 1%Pt/X%Nb-Al$_2$O$_3$ (X=1,5,10,20 is the niobia loading) catalysts were prepared by co-precipitation of the metals (Pt, Nb) in a solution containing finely dispersed alumina. The 1%Pt/X%Nb-Al$_2$O$_3$ (X=30,50) catalysts were prepared by successive impregnation using ammonium niobium oxalate (Aldrich) and tetrammineplatinium (II) nitrate (Aldrich) as precursors. The 1%Pt/Nb$_2$O$_5$ was prepared by a micro-emulsion procedure. The reaction mixture had a composition of 0.8% CO, 0.8% oxygen, and 51% H$_2$, with He as balance, and was added at a total flow rate of 195 cc/min. The reactions were carried out in a flow tubular quartz reactor equipped with an external recycle loop. Prior to the reaction, 0.2 g of catalyst was reduced at 200°C for 1 hour in pure hydrogen. Samples from the gaseous effluent were analyzed at various times using a Varian 3700 gas chromatograph equipped with a CTR I (Alltech) and a molecular sieve (Alltech) columns, mounted in parallel, and maintained at 50 °C using He as a carrier. This column arrangement allows separating H$_2$, CO, O$_2$, CO$_2$, and CH$_4$. XPS and EXAFS/XANES techniques were use to characterize the catalysts, and DRIFTS to study CO adsorption on the catalyst.

Results and Discussion

The activity of platinum niobia-promoted catalysts was measured during the preferential oxidation of CO (PROX) in a hydrogen rich flow. The results show a unique effect of niobia as a catalyst, which can either acts as a promoter or as inhibitor depending on niobia content. The most interesting result occur when Pt is supported on bulk Nb$_2$O$_5$ in which case the CO activity is significantly inhibited. XPS results showed that increasing the niobia content increases the oxidation states of Pt and Nb affecting also their binding energies. These surface changes modify the strength of CO adsorbed on Pt as shown by DRIFTS, with CO weakly adsorbing when Pt is supported on bulk Nb oxide. Operando infrared results show a shift of the linear CO band frequency to higher values as Nb loading is increased, and this band appears to be an spectator species because it does not change as CO conversion increases. Operando EXAFS/XANES and ex-situ XPS results show that the reduced Pt-Nb promoted catalysts are in a partially Pt$^{2+}$ oxidation state. In fact, in all the Nb-promoted catalysts, 40% of Pt remains as Pt$^{2+}$ when pre-reduced in hydrogen at 250°C, while unpromoted Pt/Al$_2$O$_3$ was completely reduced at the same temperature. The addition of a small amount of Nb promotes CO conversion on the 1%Pt/Al$_2$O$_3$ catalyst (Fig. 1). 100% CO conversions were obtained at 170°C on 1%Pt/5%Nb-Al$_2$O$_3$, whereas the un-promoted catalyst did not show full conversions below 200°C. On the other hand when niobia was used as a support, 1%Pt/Nb$_2$O$_5$, the selectivity to CO under PROX conditions was significantly reduced but it was still able to maintain a high activity for hydrogen oxidation.

Significance

This work shows that small amounts of Nb promote the preferential oxidation of CO, helping to completely remove the CO from H$_2$-rich stream at lower temperatures than the unpromoted Pt catalyst. Such catalysts could be applied to remove CO from H$_2$-rich fuel streams feeding proton-exchange membrane fuel cells (PEMFC).

Figure 1. PROX results on 1%Pt/X%Nb-Al$_2$O$_3$ with X=1,5,10,20% of Nb loading. The dashed line corresponds to the unpromoted 1%Pt/Al$_2$O$_3$ catalyst. A) CO conversion, B) O$_2$ conversion, C) CO Selectivity. Cat.: 0.2 g. 0.8% CO, 0.8% O$_2$, 51% H$_2$, balance He. Total flow: 195 cc/min.

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References