



## Promotion effect of support calcination on ethanol production from CO hydrogenation over Rh/Fe/Al<sub>2</sub>O<sub>3</sub> catalysts

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### ABSTRACT

A series of Rh/Fe/Al<sub>2</sub>O<sub>3</sub> catalysts, in which the Al<sub>2</sub>O<sub>3</sub> supports were calcined at different temperatures, were prepared by a sequential impregnation method. The catalysts were tested by CO hydrogenation and characterized by N<sub>2</sub> adsorption–desorption, X-ray diffraction (XRD), CO pulse chemisorption, temperature programmed surface reaction (TPSR) and temperature programmed reduction (TPR) techniques. The activity of ethanol formation was the highest when the catalyst support was calcined at 800 °C, while that of methanol formation increased continuously with the calcination temperature of the support. According to the commonly accepted mechanism of C<sub>2</sub>-oxygenates formation, CO conversion followed three separate pathways after CO dissociation, and our results suggested that the activity towards CO insertion and dissociation increased gradually with the calcination temperature, but began to decrease at 900 °C. On the other hand, direct hydrogenation of CO to methanol was still increasing at 900 °C. These observations were in agreement with TPSR results. Dispersion of the Rh or Fe species was not impaired, and even improved, with the declining of the surface area of the support due to high temperature calcination. TPR results revealed that Rh–Fe interaction was strengthened after calcination, due to a lowering in surface hydroxyl reactivity of the support and an increase of the Rh–Fe interface area. As a result, the amount of Rh–Fe–O sites for CO dissociation and insertion increased with the calcination temperature, giving rise to the increase in ethanol formation activity. However, an over-strong Rh–Fe interaction would be resulted when the catalyst support was calcined at 900 °C, and this would cause more Fe species to be reduced, which would then cover the Rh sites. Consequently, CO uptake as well as dissociation and insertion of CO would decrease, leading to more CO molecules being hydrogenated directly to methanol, thus causing a decrease in the selectivity of ethanol formation.

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### 1. Introduction

The search for processes to provide alternative feedstock for chemicals and fuels has been promoted by the potential shortage of traditional petroleum reserves, as well as the increasing instability of international crude oil resources and foodstuff supply [1,2]. Direct catalytic hydrogenation of CO is one of the most promising technologies for the production of liquid fuels and chemicals from syngas, which can be derived from coal, natural gas, or biomass. Among the potential end products of coal/biomass gasification, ethanol is particularly attractive because of its prospect as a clean alternative fuel, a gasoline blend, as well as a hydrogen carrier [3]. Accordingly, extensive recent research

and development in syngas conversion have been dealing with ethanol synthesis, both experimentally [4–8] and theoretically [9,10].

Since the pioneering work of Union Carbide in 1975 [11,12], Rh-based catalysts have been known to be the most efficient ones in the synthesis of C<sub>2</sub>-oxygenates (ethanol, acetaldehyde and acetic acid) from CO hydrogenation due to their unique CO adsorption behavior [13,14]. The effect of the support on the selectivity towards C<sub>2</sub>-oxygenates has been thoroughly investigated [15]. SiO<sub>2</sub> has been the most frequently used support, since Rh-based catalysts supported on it usually exhibit moderate activity and good selectivity towards C<sub>2</sub>-oxygenates during CO hydrogenation [16], but its performance depends on the properties of the silica employed. For instance, trace amounts of impurities in the SiO<sub>2</sub> will lead to distinctly varying catalytic properties of the corresponding Rh-based catalyst [17]. Therefore, a great deal of time-consuming work has to be carried out on the pretreatment of SiO<sub>2</sub>. Also, the precise optimization of the loading of the Rh component and other promoters is a necessity [18].

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Al<sub>2</sub>O<sub>3</sub> has been reported to have much higher concentration of reactive surface hydroxyls than silica [19], which would lead to lower sensitivity to catalyst impurities, as surface hydroxyls can react with the metal impurities and convert these into non-active species on the support. However, literature references are scarce for Rh supported on Al<sub>2</sub>O<sub>3</sub>. Burch and Hayes [20] reported an ethanol selectivity of 50% over a 2%Rh-Fe/Al<sub>2</sub>O<sub>3</sub> catalyst, and Ojeda et al. [21] have also studied an Al<sub>2</sub>O<sub>3</sub>-supported 3%Rh catalyst, promoted by Mn, for CO hydrogenation to C<sub>2</sub>-oxygenates. All these catalysts, however, displayed low activities or low yields of C<sub>2</sub>-oxygenates. One of the reasons may be that a stronger interaction between Rh (or promoter) and the support occurred due to the more active surface of the Al<sub>2</sub>O<sub>3</sub>. As a result, part of Rh species could not be reduced or be reduced completely at higher temperatures, thus leading to a lower Rh dispersion or yielding larger Rh particles [22]. Therefore, for the Al<sub>2</sub>O<sub>3</sub> support, higher Rh or promoter loadings have to be used to achieve comparable activities to the silica-supported catalysts, so that very low Rh efficiency was resulted. However, these undesirable effects of the support on the dispersion and reducibility of the catalyst can be probably minimized if the properties of support, such as its texture, crystal phase and surface properties, etc. are controlled, for instance, by hydrothermal treatment in a certain medium [23,24].

It is widely accepted that the promoter/Rh boundary plays a key role in generating the required active sites for the selective synthesis of C<sub>2</sub>-oxygenates [20,21,25]. In order to optimize the Rh-promoter interface, it is thought that the use of a support that can produce a closely packed layer of deposited metal oxide would be of advantage [20]. Al<sub>2</sub>O<sub>3</sub> tends to form a closely packed monolayer of the supported metal oxide phase due to its high concentration of reactive surface hydroxyls [19]. The hydroxyl population affects the particle size of the supported metal, while the hydroxyl concentration may affect the interaction between neighboring cations or atoms on the support [20].

Fe, as a promoter for Rh-based catalysts for CO hydrogenation, has been extensively studied. It has shown interesting promoting effects for giving higher ethanol yields. A number of explanations have been made to interpret the promotion role of Fe: boosting the hydrogenation of acetaldehyde to form ethanol [26], stabilizing an acyl species, impeding CO dissociation or adsorption [27], and so on. Recently, it has been shown that Fe could stabilize adsorbed CO on both the charged and neutral Rh moieties [28]. However, no agreement regarding the promoting mechanism of Fe has been arrived yet, and this may be due to different recipes, the different preparations and reaction conditions employed, thus leading to different Fe chemical states, and displaying different effects in the CO hydrogenation reaction [29]. The chemical states of Fe are closely related to the interactions among the Fe, the Rh and the support.

Based on the idea that the surface hydroxyls of the support influence greatly the properties of the supported metal component, Al<sub>2</sub>O<sub>3</sub> was calcined at different temperatures to modify its surface hydroxyl reactivity before using it as a support in this work. Subsequently, the calcined Al<sub>2</sub>O<sub>3</sub> was impregnated with a Fe(NO<sub>3</sub>)<sub>3</sub> methanol solution prior to the incorporation of Rh component to the support, which has the effect of preventing the Rh species from migrating into the bulk of the support during the final calcinations process. Then, CO hydrogenation performance of the catalysts was correlated with the interaction extents among Rh, Fe and Al<sub>2</sub>O<sub>3</sub>, mainly monitored by means of TPSR and TPR characterizations.

## 2. Experimental

### 2.1. Catalyst preparation

Rhodium chloride was provided by Johnson Matthey Precious Metal Company. The alumina was a commercial high purity

(99.26%)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (20–40 mesh) supplied by Shangdong Chemical Plant, China. Prior to impregnation, the alumina was calcined at different temperatures (400–900 °C) for 5 h. After that the support was contacted with methanol solution of Fe(NO<sub>3</sub>)<sub>3</sub> with appropriate concentration until methanol evaporated completely. The promoter-support precursor was then dried at 110 °C for 4 h. The introducing of Rh to the promoter-support precursor was achieved by sequential impregnating and drying of Fe/Al<sub>2</sub>O<sub>3</sub> with a RhCl<sub>3</sub> aqueous solution. The as-prepared catalyst was dried at 50 °C for 4 h, and then at 110 °C for 4 h before the final air calcinations in air at 500 °C for 4 h in a muffle furnace. The finish catalyst samples were denoted as Rh/Fe/AT, where T was the calcination temperature of Al<sub>2</sub>O<sub>3</sub> (A). The Rh and Fe loadings were both 2 wt% in all samples, and the molar ratio of Rh:Fe was 1:1.84.

### 2.2. Activity measurement

CO hydrogenation reactions were carried out on a high-pressure fixed bed stainless steel microreactor (300 mm length and 6.0 mm inner diameter). The catalyst samples (ca. 0.70 g and 1.0 ml) were reduced at 350 °C (heating rate 2 °C/min) for 2 h by 5 l/h H<sub>2</sub> before the reaction. The reactor was then cooled down to 280 °C and the gas flow was switched to syngas ( $n(\text{H}_2)/n(\text{CO})=2$ , 12.5 l/h), and the time on stream was 4 h under 5.0 MPa. The reaction effluent then passed through a condenser filled with cold de-ionized water, so that the oxygenate products were dissolved in the de-ionized water. The aqueous solution containing the oxygenates was analyzed off-line by a Varian CP-3800 gas chromatograph with a FFAP column using an FID detector and with 1-pentanol as an internal standard. The tail gas was analyzed on-line by a Varian CP-3800 GC with a Porapak QS column and a TCD detector.

The conversion of CO was calculated basing on the fraction of CO that has formed carbon-containing products according to the following equation:

$$\text{Conversion (100\%)} = \frac{\sum n_i \times M_i}{M_{\text{CO}}} \times 100$$

The selectivity to product *i* was calculated basing on the total number of carbon atoms in the product, and was defined as:

$$S_i(\text{100\%}) = \left( \frac{n_i M_i}{(\sum n_i M_i)} \right) \times 100$$

The space time yield of methanol or ethanol was calculated as:

$$\text{STY} = \frac{W_p}{W_c t}$$

In the above-mentioned formulas,  $n_i$  was the number of carbon atoms in product *i*,  $M_i$  was the percentage of product *i* detected,  $M_{\text{CO}}$  was the percentage of CO in the syngas feed,  $W_p$  and  $W_c$  were the weights of product formed and catalyst used, respectively, and  $t$  was the reaction time (h). Error analysis was estimated in the range of 5–8% in all of the data collection.

### 2.3. Catalyst characterization

The BET surface area and pore volume of Al<sub>2</sub>O<sub>3</sub> were obtained using N<sub>2</sub> adsorption–desorption isomers at –196 °C in a Micromeritics ASAP 2020 apparatus. Prior to N<sub>2</sub> adsorption, the sample was degassed under vacuum at 150 °C for 2 h.

A PAN analytical X'Pert PRO X-ray diffractometer equipped with Cu K $\alpha$  1 was employed for the collection of XRD patterns of catalyst samples in the 2 $\theta$  range of 10–90°.

CO uptakes as well as TPSR and TPR experiments were performed on a Micromeritics Autochem 2910 apparatus. TPR experiments were carried out with a flowing 10% H<sub>2</sub>/Ar gas mixture at a

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