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Short Communication

The effects of oxidation–reduction treatment on the structure and activity of cobalt-based catalysts

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ABSTRACT

This study reports the effects of oxidative-reductive (OR) treatment on 10 wt% Co/Al_2O_3 and 0.25 wt% Ru-10 wt% Co/Al_2O_3 catalysts. Temperature-programmed analysis revealed that the cobalt in both catalysts became more reducible with increase number of OR treatment. A reduction–oxidation–reduction treatment increased Co surface area and dispersion of the $Ru\text{-}Co/Al_2O_3$ catalyst from 7.6 to 10.1 m^2/g and from 14.9% to 17.3%, respectively. The treatment also increased the CO conversion from 21% to 36% and accompanied a small increase in CH_4 selectivity in Fischer–Tropsch synthesis experiments. However, the effect of OR treatment on the Co/Al_2O_3 catalysts was insignificant.

1. Introduction

Fischer–Tropsch synthesis (FTS) proceeds on the surface of cobalt metal particles that are dispersed on an oxide support. In general, a cobalt FTS catalyst is activated by fully reducing the cobalt into the metallic form by H_2 and/or CO prior to the reaction [1–3]. It was demonstrated that the catalytic activity of some transition metals for hydrogenation reaction could be enhanced by oxidation–reduction (OR) treatment [4]. The effect of cyclic OR treatment on cobalt based catalysts for FTS was first reported by Kobylinski et al. [5], who demonstrated that the CO conversion rate in an FTS process could be increased by a factor of two when alumina supported Co or Co-Ru catalysts was subjected to repeated OR treatments. Iglesia et al. [6] observed that a significant amount of Ru metal migrated into the bulk of Co during the oxidation steps when the catalyst was subjected to a cyclic OR treatment. They concluded that a close interaction between Co and Ru was important to warrant an effective synergy of the bimetallic precursors. Jacobs et al. [7] reported that OR treatment applying to a 2 wt% Ru-15 wt% Co/Al_2O_3 sample facilitated the sintering of metallic cluster to form large size and to promote mixing in nanometric level. Recently, a combined TEM/XPS study using Pt and Ru promoted cobalt catalysts suggested that the oxidation led to the segregation of the promoter and cobalt with the promoter being encapsulated by Co_3O_4. Reduction of this state resulted in a decrease of the surface concentration of the promoter [8].

The focus of this study is to correlate the structural properties, in particular the state of the Co metal, with the cyclic OR treatment. The properties of 10.0 wt% Co/Al_2O_3 and 0.25 wt% Ru-10.0% wt Co/Al_2O_3 catalysts before and after different numbers of OR cycles were characterised and their catalytic performance for FTS were then tested.

2. Experimental

2.1. Catalyst preparation

The Co/Al_2O_3 was prepared by incipient wetness impregnation. An aliquot of $Co\ (NO_3)_2 \cdot 6H_2O$ dissolved in acetone was added to a known amount of alumina support. The sample was dried at 110 °C overnight and then calcined at 450 °C for 2 h. The Ru promoted Co/Al_2O_3 catalyst was prepared by impregnating the calcined Co/Al_2O_3 with a ruthenium chloride solution.

2.2. Oxidation–reduction treatment of catalysts

The reduction segment involved the reduction in a flow of 10% H_2/Ar up to 350 °C at a ramping rate of 5 °C/min. The dwell time was 2 h. For the oxidation segment, the reduced sample was oxidised in a flow of 5% O_2/He from 50 °C to 280 °C at a ramping rate of 5 °C/min. The dwell time was 30 min. After OR treatment, all samples were passivated under a flow of 2% O_2/He before further characterisation. The treatment applied to the sample that was reduced but subjected to no OR cycle was denoted as R, and those subjected to 1, 2 and 3 OR cycles were denoted as ROR, $R(OR)_2$ and $R(OR)_3$, respectively.

2.3. Catalyst characterisation

TPR analysis was conducted in a Micromeritics AutoChem 2950HP analyser. Twenty-five milligrams of sample was dried in argon at 110 °C and cooled to 50 °C. It was then heated in a flow of 10% H_2/Ar

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to 850 °C at a rate of 5 °C/min and held at this temperature for 30 min. The cobalt surface area of samples was determined from CO chemisorption. One hundred milligrams of sample was first subjected to the $R(OR)_n$ treatment as described in Section 2.2 followed by helium purging for 30 min at 350 °C before the temperature was decreased to 50 °C. At this temperature, a series of pulses containing fixed volume of CO were injected to the sample chamber and the change in CO concentration was recorded. To measure the percentage reduction of a sample, the reduced sample was purged in He for 1 h at 350 °C. It was then determined by measuring the amount of oxygen consumed in a pulse oxidation analysis at 280 °C, based on the assumption that Co^0 was oxidised to Co_3O_4. The dispersion and the particle size of cobalt were then calculated after correction of the percentage reduction of Co as reported by Bartholomew et al. [9]. A stoichometry ratio of 1 was used in the calculation. X-ray photoelectron spectroscopy (XPS) measurement was carried out in an ESCALAB250Xi (Thermo Scientific, UK) with a mono-chromated Al Kα source. Binding energies were calibrated using the C 1 s peak at 285.0 eV.

2.4. Fischer–Tropsch synthesis experiments

FTS experiments were carried out in a fixed bed reactor at 220 °C and 20 bar. 1 g of catalyst was mixed with 2 g of α-alumina. The syngas flow rate was 100 ml/min with the gas composition of H_2:CO:Ar being 2:1:3. For the R-treated catalyst, the catalyst was reduced at 450 °C for 16 h using 5% H_2/Ar. For the ROR-treated catalyst, the catalyst was first reduced at 450 °C for 16 h followed by oxidation at 250 °C for 4 h with 10%O_2/Ar, and a further reduction was carried out at 350 °C for 16 h. These treatment conditions were chosen to achieve significant conversions during FTS experiments for comparing the catalytic activity Co/Al_2O_3 and $Ru\text{-}Co/Al_2O_3$. Gaseous products were analysed by an online gas chromatography (Perkin Elmer GC-500). All reported data were measured at steady state after 24 h on stream.

3. Results and discussion

3.1. Reduction characteristics of freshly prepared catalysts

Fig. 1 shows the 10.0 wt% Co/Al_2O_3 catalyst exhibited two peaks upon reduction. The first reduction occurred at 344 °C, and the second emerged as a broader peak at 535 °C. The reductions of Co_3O_4/CoO and CoO/Co are the main contributions to the two reduction peaks, although the corresponding reduction temperature may change depending on the choice of cobalt precursors and the supporting materials [10].

Two peaks indexed at 273 °C and 423 °C were observed for $Ru\text{-}Co/Al_2O_3$, which suggested the promoting effect of ruthenium for the reduction of cobalt species. A small reduction peak was also detected at 134 °C, which could be due to the reduction of the small amount of ruthenium oxide present in the sample. The reduction of Ru was reported occurring at 140 °C when it was supported on alumina [11,12]. When the metallic Ru was formed at low temperature, it would facilitate the dissociation of the hydrogen molecules and provide spillover hydrogen for cobalt reductions. This enhanced the overall reduction process of cobalt as indicated by the lower reduction temperatures of cobalt oxides [13].

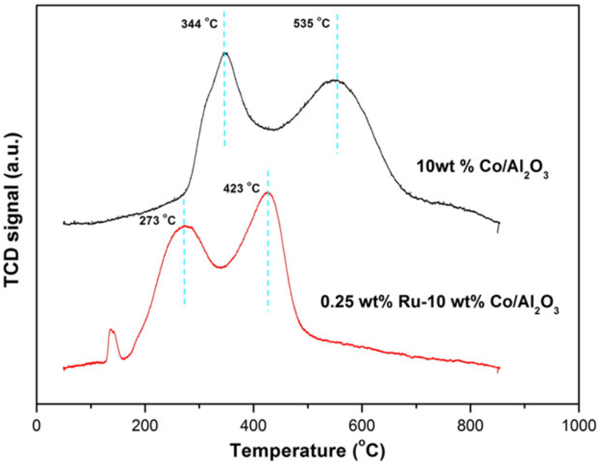

Fig. 1. TPR profiles of freshly calcined samples.

3.2. Effects of OR cycles on the reduction profiles of catalysts

The effects of OR cycles on the reduction profile for both Co/Al_2O_3 and $Ru\text{-}Co/Al_2O_3$ are illustrated in Fig. 2. The reduction represented by each profile was performed between 50 °C and 350 °C, and therefore, complete reductions of these samples were not achieved under this condition. However, the oxidation step that immediate followed the reduction was able to completely oxidise the sample to the Co_3O_4. As a result, all reduction analysis starts with the same oxidisation state of sample.

It was found that when Co/Al_2O_3 was subjected to repeated OR treatment, the reductions temperatures shifted to lower values from 344 °C, 291 °C, 283 °C to 268 °C (Fig. 2(a)). The peak intensity and peak area that represented the amount of H_2 consumed during reduction lowered with increasing number of OR cycles. The tailing of the TCD signal also suggested that reduction was likely to continue after 2 h reduction. The low percentage of reductions (less than 20%) are given in Table 1.

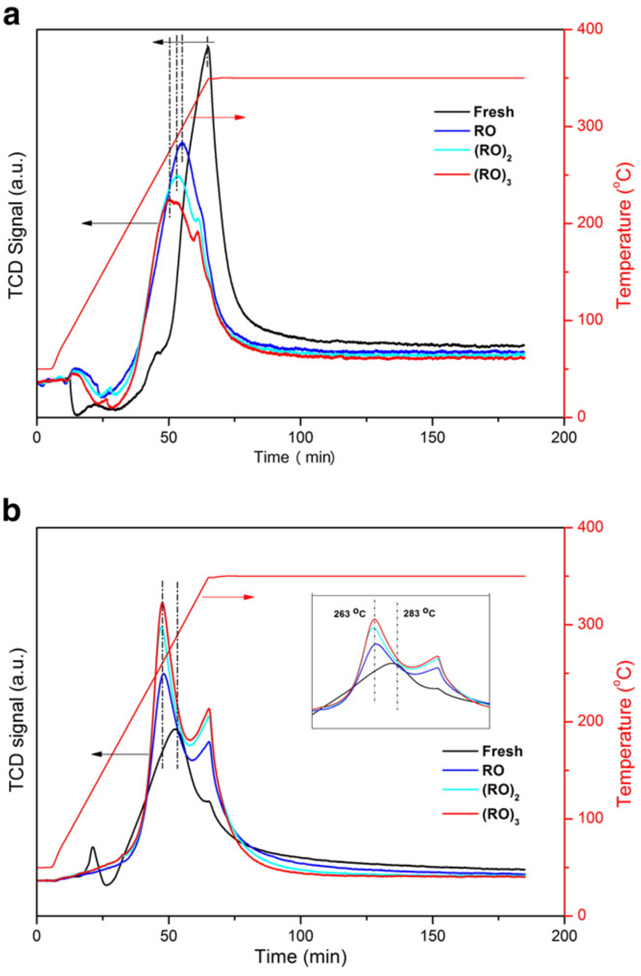

Fig. 2. Effect of OR cycles on the reduction profile of (a) Co/Al_2O_3 and (b) $Ru\text{-}Co/Al_2O_3$.