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Optimization of the pretreatment procedure in the design of cobalt silica supported Fischer–Tropsch catalysts

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Abstract

The effect of cobalt precursor, catalyst pretreatment and promotion with ruthenium and rhenium on the formation of cobalt metal nanoparticles and catalytic performance of supported Fischer–Tropsch (FT) catalysts was studied using a combination of techniques (DSC–TGA, UV–vis spectroscopy, XPS, XRD, EXAFS–XANES, in situ magnetization measurements, propene chemisorption and catalytic measurements). The cobalt promoted and unpromoted catalysts were prepared by aqueous co-impregnation using cobalt nitrate or acetate, ruthenium nitrosyl nitrate or perrhenic acid. In both unpromoted and Ru and Re-promoted cobalt catalysts after impregnation and drying, cobalt is present mainly in octahedrally coordinated complexes. The repartition of cobalt species between Co_3O_4 and cobalt silicate depends essentially on the exothermicity of precursor decomposition. Cobalt nitrate precursor, with an endothermic decomposition, favors Co_3O_4 crystallites. Lower temperature of cobalt nitrate decomposition and catalyst calcination generally leads to higher dispersion of supported cobalt oxide. Cobalt acetate precursor, with an exothermic decomposition, favors cobalt silicate. By optimizing the conditions of cobalt acetate decomposition, the fraction of cobalt silicate can be decreased favoring a more reducible Co_3O_4 phase. For the catalysts prepared from cobalt nitrate, promotion with ruthenium increases the cobalt dispersion, while maintaining high reducibility. For the catalyst prepared via low temperature decomposition of cobalt acetate, addition of ruthenium increases the fraction of Co_3O_4 crystalline phase and decreases the concentration of barely reducible cobalt silicate. The Fischer–Tropsch reaction rates over unpromoted and promoted cobalt catalysts were found to be primarily a function of the number of cobalt metal sites, which are generated by the reduction of Co_3O_4 crystallites.

Keywords: Fischer–Tropsch synthesis; Cobalt catalysts; Cobalt silicate; Nanoparticles; Promoters; Oxidative pretreatment

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1. Introduction

Fischer–Tropsch (FT) synthesis is a part of gas-to-liquids (GTL) technology, which produces clean fuels from natural gas. FT synthesis has become more attractive as the discovered reserves of natural gas are approaching those of crude oil. The catalysts for the conversion of syngas generated in GTL plants are usually based on metallic cobalt dispersed on an oxide porous support (i.e. silica) and promoted with the small amounts of noble metals [1]. It has been shown that both catalyst activity and hydrocarbon selectivity are functions of the density of cobalt metal sites. The cobalt site density depends on both cobalt dispersion and reducibility. Higher concentrations of cobalt metal sites typically favor higher FT reaction rates [2]. The hydrocarbon selectivities generally follow Anderson–Schulz–Flory (ASF) polymerization sequence with deviations, which are likely to be attributed to the secondary reactions (olefin readsorption, oligomerisation, cracking, isomerisation) [3]. It is generally suggested that promotion of cobalt FT catalysts with noble metal increases the number of metal sites due to the enhanced cobalt reducibility [4,5]. Very little information is available however, about the effect of

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promotion with noble metals on the mechanism of oxidative decomposition of cobalt precursors. The specific goal of this paper is to demonstrate that different catalytic performance of cobalt monometallic and bimetallic catalysts could be attributed not only to the better cobalt reducibility but also to the different structure of cobalt species generated by the oxidative decomposition of cobalt precursors.

2. Experimental

2.1. Catalysts preparation

The cobalt catalysts were synthesized via incipient wetness impregnation or co-impregnation using aqueous solutions of cobalt nitrate or acetate. Cab-osil M-5 fumed silica ($S_{\mathrm{BET}} = 214\ \mathrm{m}^2/\mathrm{g}$) was used as catalytic support in all catalyst preparations. Prior to impregnation Cab-osil M5 was agglomerated by wetting and dried at 373 K. The precursors of promoters are ruthenium nitrosyl nitrate in HNO_3 (Ru = 1.5 wt.%) or perrhenic acid. They were used as a co-impregnating salt for preparation of promoted catalysts. The contents of cobalt and promoting noble metal in the catalysts were, respectively, 8–10 and 0.1–0.4 wt.% (Table 1). The impregnated catalysts were dried, calcined in a flow of air at different temperatures (443–673 K) and then reduced in hydrogen at 673 K for 5 h.

2.2. Characterization techniques

Simultaneous differential scanning calorimetry (DSC) and differential thermogravimetric analysis (TGA) of catalyst precursors were carried out in an air flow at heating rate of 1 K/min using a DSC–TGA SDT 29S thermal analyzer. Diffuse reflectance UV–vis spectra for catalysts were obtained under ambient conditions with a Varian–Cary 4 spectrophotometer. X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer and Cu Kα radiation. The average size of Co_3O_4 crystallites was determined by Scherrer equation using (4 4 0) peak at $2\theta = 65.3^{\circ}$. X-ray absorption measurements (XANES and EXAFS) were carried out at the European Synchrotron Radiation Facility (Grenoble, France) on the DUBBLE-CRG beamline. X-ray photoelectron surface analysis of the reduced catalysts was performed with a VG ESCALAB 220XL spectrometer. The reduction of oxidized catalysts was carried out in pure hydrogen at 673 K for 5 h in the reactor chamber of the XPS spectrometer. After the reduction, the sample was transferred to the analysis chamber. The extent of reduction was evaluated from decomposition of XPS spectra of the reduced catalysts as described in ref. [6]. The in situ magnetization measurements of cobalt catalysts during their reduction were carried out in the reactor, which was simultaneously a vibrating magnetometer cell [7]. This setup allows in situ monitoring of sample magnetization during standard temperature-programmed experiments in pure hydrogen.

The relative number of metallic sites in the reduced catalysts was evaluated using propene chemisorption. More information about propene chemisorption over cobalt catalysts is available elsewhere [8]. The catalytic behavior in FT synthesis was studied in a fixed bed microreactor using synthesis gas with a H_2/CO ratio 2 at atmospheric pressure. The catalysts were reduced (673 K, 5 h) in situ before starting a catalytic test. The FT reaction rates and hydrocarbon selectivities were evaluated after 24 h on-stream. The FT reaction rates (cobalt time yields) were calculated from carbon monoxide conversions and gas hourly space velocities; then they were normalized by the number of cobalt atoms loaded in the reactor.

3. Results and discussion

3.1. Impregnated and dried catalysts

The UV–vis spectra (not shown) of impregnating cobalt nitrate and cobalt acetate solutions with and without Ru and Re promoters exhibit a broad band at 510 nm, which is in agreement with previous report [9], was assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition in octahedral high-spin Co^{2+} complexes. The broad band at 510 nm remains intense in the impregnated and dried samples. This suggests octahedral coordination of cobalt ions in the impregnating solutions and after deposition on silica.

Table 1
Characterization of cobalt silica supported catalysts

Catalysts	Cobalt content (wt.%)	Ru or Re content (wt.%)	$T^{\circ}_{\mathrm{calcination}}$ (K)	Size of Co_3O_4 crystallites from XRD (nm)	ICo_{2p}/ISi_{2p} ratio (XPS) in the oxidized samples	Fraction of Co° in the reduced catalysts from XPS (%)	Propene chemisorption (μmol/g)
CoAc673	9.5	0	673	–	1.6	11	1.2
CoAc443	9.5	0	443	–	2	26	12.9
CoN673	9.8	0	673	20	0.33	60	22.1
CoN423	9.8	0	423	12	0.7	65	26.1
RuCoN673	8.1	0.04	673	12	0.7	54	50.1
RuCoAc673	7.6	0.02	673	–	2.2	17	5.3
RuCoAc443	7.4	0.1	443	–	2.1	31	49.6
ReCoAc673	7.1	0.4	673	–	2.3	14	14.2

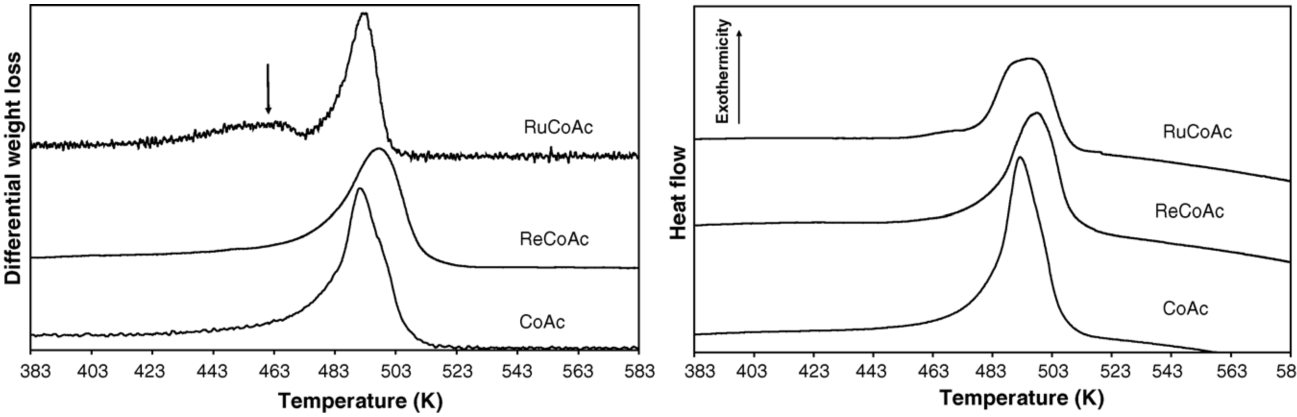

Fig. 1. Differential weight loss of the impregnated and dried catalysts prepared from cobalt acetate (left); heat flow recorded during weight loss (right). Temperature ramp = 1 K/min.

3.2. Decomposition of cobalt precursors

The DSC–TGA data suggest that decomposition of cobalt nitrate is endothermic and proceeds at 423 K, whereas decomposition of cobalt acetate was highly exothermic and proceeds at 493 K (Fig. 1). Co_3O_4 is the product of decomposition of both pure cobalt nitrate and cobalt acetate salts in air [6]. Carbon dioxide and nitrogen dioxide were, respectively, the major gaseous products released during cobalt acetate and cobalt nitrate decomposition. Addition of Re or Ru does not modify to any noticeable extent the DSC–TPR curves of the catalysts prepared from cobalt nitrate. With the catalysts prepared from cobalt acetate, which were promoted with ruthenium, an additional DSC–TGA peak was observed at lower temperatures during cobalt acetate decomposition (Fig. 1). The chemical analysis confirmed previous observations for cobalt ruthenium catalysts about the volatility of ruthenium oxides on heating in oxidizing atmosphere [10]. Indeed, Table 1 indicates a significant loss of ruthenium after calcination of cobalt-ruthenium catalysts at 673 K.

Our data show that varying cobalt precursors and conditions of their decomposition leads to cobalt catalysts with very different cobalt species. Co_3O_4 was the dominant phase in both unpromoted and Ru and Re promoted catalysts prepared from cobalt nitrate (Table 1). Co_3O_4 particles were detected in these catalysts by XRD, XANES–EXAFS and UV–vis spectroscopy (bands at 450 and 730 nm).

Very-low intense Co_3O_4 diffraction peaks were detected in the catalysts prepared from cobalt acetate. This suggests very low concentration of Co_3O_4 crystalline phase in these catalysts. XANES–EXAFS shows that α-cobalt silicate type species could be the major phase present in the unpromoted cobalt and promoted catalysts after cobalt acetate decomposition [6]. It is shown however, that the temperature of decomposition of cobalt acetate produces a strong impact of the cobalt repartition between cobalt acetate and cobalt oxide. No Co_3O_4 is observed after the oxidative pretreatments at high temperatures (>493 K). When the decomposition of cobalt acetate was conducted at lower temperatures, some concentration of Co_3O_4 phase was detected by XPS, XAS and UV–vis spectroscopy. Addition of ruthenium results in a further increase in the concentration of Co_3O_4 in the catalysts obtained via low temperature decomposition of cobalt acetate. The moduli of Fourier transform of EXAFS for promoted cobalt catalysts are displayed in Fig. 2. The Fourier transform modulus shifts from that typical of Co_3O_4 (RuN673) to that more characteristic of cobalt silicate (ReAc673). In contrast to RuAc673, the cobalt catalyst prepared by low temperature decomposition of cobalt acetate (RuAc443) displays the Fourier transform modulus, which clearly indicates the presence of some concentration of Co_3O_4 phase.

3.3. Reduced catalysts

The XPS experiments indicate that the extent of cobalt reduction depends on cobalt precursors, promotion with ruthenium or rhenium and calcination temperature (Table 1). The cobalt nitrate catalysts are generally more reduced than the cobalt acetate ones. Lower temperature of decomposition of cobalt acetate increases the extent of cobalt reduction

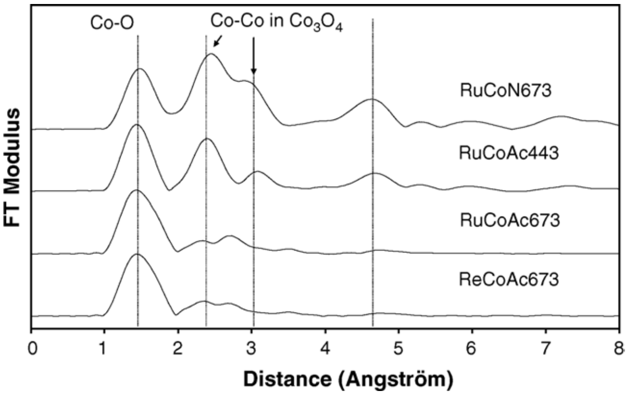

Fig. 2. Moduli of Fourier transform of EXAFS for oxidized promoted cobalt catalysts.

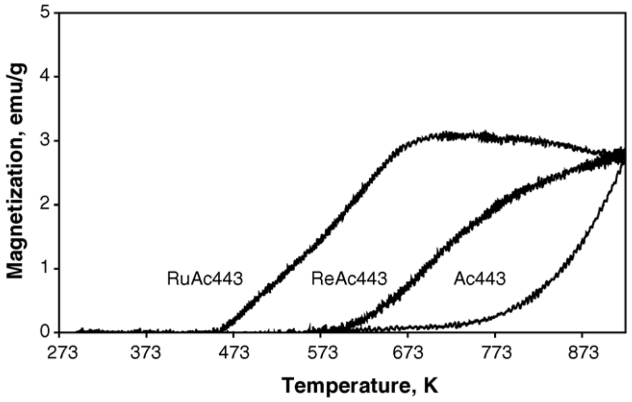

Fig. 3. In situ magnetization curves of cobalt catalysts measured during temperature-programmed reduction in pure hydrogen (temperature ramp = 12 K/min). The catalysts were prepared via decomposition of cobalt acetate at 443 K.

relative to the catalysts prepared from cobalt acetate and precalcined at 673 K.

Addition of Re and especially Ru also considerably improves cobalt reducibility (Table 1). The in situ magnetic method, which is selectively sensitive to the metal particles, showed higher concentration of cobalt metal phase during the reduction of promoted cobalt catalysts in pure hydrogen (Fig. 3). The effect of the promotion on cobalt reducibility is more pronounced for the catalysts prepared from cobalt acetate promoted with ruthenium (Fig. 3) and for the catalysts prepared from cobalt nitrate which were precalcined at low temperatures (Table 1). After the high temperature pretreatment in oxidizing atmosphere, the effect of ruthenium on cobalt reducibility is much smaller which is probably due to a considerable loss of ruthenium due to the sublimation of supported ruthenium oxides [10].

3.4. Catalytic performance

Catalytic data of cobalt catalysts are presented in Table 2. The FT reaction rate was a function of cobalt metal sites in the catalysts measured by propene chemisorption (Fig. 4). The catalysts prepared from cobalt nitrate are generally more active than those prepared from cobalt acetate. In line with the concentration of reducible Co_3O_4 phase and the number of cobalt metal sites, Table 2 shows that lower temperature of decomposition of cobalt acetate improves catalytic performance. Addition of ruthenium and rhenium also results in an increase in FT reaction rate. The effect of promotion on catalytic performance was more noticeable for the catalysts prepared from cobalt acetate. The C5+ selectivity and chain growth probabilities (α) for both unpromoted and promoted cobalt catalysts vary, respectively, between 36 and 70%, and 0.65 and 0.85%.

Table 2
Catalytic performance of cobalt catalysts

Catalysts	FT reaction rate (10^{-4} s^{-1})	C5+ selectivity	α
CoAc673	0.01	70	0.76
CoAc443	0.7	60	0.73
CoN673	2.9	70	0.78
CoN423	3.7	62	0.85
RuCoN673	6.1	56	0.73
RuCoAc673	1.0	36	0.65
RuCoAc443	4.0	56	0.73
ReCoAc673	2.3	40	0.66

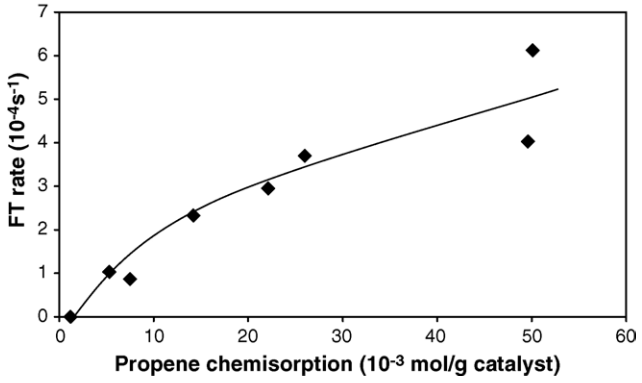

Fig. 4. FT reaction rate on promoted and unpromoted cobalt catalysts as a function of propene chemisorption.

4. Conclusion

Isolated octahedrally coordinated Co^{2+} complexes were detected by several spectroscopic techniques in the monometallic and bimetallic catalysts after deposition of a cobalt precursor and the promoters. During oxidative decomposition of a cobalt precursor, these complexes could either agglomerate into small crystallites of Co_3O_4 or react with silica yielding the species with cobalt local coordination similar to that in α-cobalt silicate. The oxidative decomposition of cobalt nitrate is endothermic, whereas the decomposition of cobalt acetate is exothermic. In both unpromoted and promoted catalysts, the endothermicity of cobalt nitrate decomposition favors Co_3O_4 crystallites. Co_3O_4 crystallites can be then reduced to cobalt metal particles, which provide active metal sites for FT reaction. The exothermicity of cobalt acetate decomposition leads to cobalt silicate type species, which do not produce active sites after the reduction. The concentration of amorphous cobalt silicate can be minimized by efficient control of the heat released during decomposition of cobalt acetate.

Cobalt-ruthenium catalysts prepared from cobalt nitrate exhibit a higher FT rate than the monometallic counterpart. Characterization data suggest (Table 1) that promotion with ruthenium significantly increases the dispersion of cobalt oxide. Both unpromoted and promoted cobalt catalysts prepared from cobalt nitrate exhibit high extent of reduction after treatment with hydrogen at 673 K. Higher catalytic activity of these catalysts was principally attributed to higher cobalt dispersion, and thus, higher concentration of cobalt metal sites. Some enhancement in cobalt reducibility due to the presence of ruthenium was observed for the cobalt catalysts precalcined at relatively lower temperatures (373 K). Chemical analysis data (Table 1) suggest that ruthenium oxides sublime at higher temperatures and thus ruthenium can not significantly enhance the reducibility of the catalysts which were submitted to high temperature oxidizing pretreatments.

Promotion with ruthenium of the catalysts obtained from cobalt acetate increases the concentration of Co_3O_4 crystallites and reduces the amount of cobalt silicate. DSC–TGA studies have shown that in the catalysts promoted with ruthenium cobalt acetate decomposes in a much broader temperature range and at lower temperatures than in monometallic catalysts (Fig. 1). Lower concentration of cobalt silicate in the Ru promoted catalysts pretreated at lower temperatures could be attributed to a much softer decomposition of cobalt acetate and, therefore, smaller heat release in the presence of ruthenium. The propene chemisorption has shown a spectacular growth in the number of cobalt metal sites in these catalysts after the reduction. A 5–10 times increase in the FT reaction rate relative to monometallic catalyst prepared from cobalt acetate has been also observed. Modification of cobalt catalysts with rhenium produces a much smaller effect on decomposition of cobalt acetate, on the number of cobalt metal sites and on FT catalytic behavior relative to the catalysts promoted with ruthenium.

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