



## Effect of strain on the performance of iron-based catalyst in Fischer-Tropsch synthesis

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### ABSTRACT

The role of strain on metal catalysis has been widely investigated by theoretical calculations. It is hard to prove by direct experimental strategies. In this work, we show how the strain can be adjusted experimentally to modulate Fischer-Tropsch synthesis (FTS) activity. The strain value is derived from the X-ray diffraction (XRD) line broadening method. The d-band occupancy ( $n_d$ ) is calculated semi-quantitatively by magnetic characterization on a vibrating sample magnetometer (VSM). A volcano curve is correlated between strain and FTS activity. The combination of physical property such as mechanics, magnetization, hardness and density functional theory (DFT) calculations is proposed to elucidate a general strain induced reactivity behavior. Such a strain dependent behavior is related to the variation in d-band electronic property of the metal.

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### 1. Introduction

The role of strain in tuning metal surface catalysis has developed rapidly over the past decade [1–7], including hydrogenolysis reaction, oxygen reduction reaction, methanol synthesis and methanation reaction. Three fundamental factors have been identified in theoretical literatures as playing a crucial role in strain mediated surface chemistry: band coupling [8], mechanical work [9,10] and surface tension mediated charge effects [11,12]. Strain induced variations in the d-band structure influence adsorbate-metal bonding state through the adsorbate valence orbital with metal d orbital band coupling. The coupling of the applied stress field to the adsorbate-induced relaxation (a strain field) brings about a distinct mechanical work term. Moreover, the strain induced shifts in the electrode potential or adsorption enthalpy mediated by the surface tension affect the energy of charged species, most readily demonstrated in electrochemistry [11,13]. Generally, strain in metal can be introduced by ball-milling [14], doping [15–17], alloying [18–20], adding template agent [6,21], exerting high pressure [22] and ion sputtering [2]. These methods

modify the structure through a combination of plastic deformation and elastic strain. The elastic strain emerges along with applied external forces. The plastic deformation is manifested in lattice defect, such as dislocations and magnetostriction. This type of strain is often called residual strain (the strain remaining in a body after the additional stress has been removed, and the retained portion is as strain associated with dislocations). Dislocations emit at a surface where they present step-like structures. These steps are preferential adsorption sites on a catalyst for the adsorbed molecular species [23,24]. In fact, the correlation between strain and the adsorption energy on various metals has been confirmed by density functional (DFT) calculations.

To gain insight into the theory by experimental strategies, researchers have investigated the strain effect on single crystal [1] or metal catalysts [25]. Nevertheless, the single crystal model deviates from the real catalysis environment. Other researchers have involved the conventional supported metal catalysts, which introduce the strain indirectly, and also contain complex factors, such as strong metal-support interaction (SMSI), dispersion, porosity and particle size effect. Curtin and Francis [10] reported the possibility of using strain as a tool to achieve continuous control over methanation reactivity over Ni, Ni<sub>3</sub>Fe, NiFe catalysts. The experimental work performed by Fernandez et al. involved strain-enhanced activity for Ni-based ethane hydrogenolysis

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reaction, which introduce microstrain via the local deformation caused by the interaction between metal and the graphene edges [21]. Strasser et al. [26] adopted a core-shell nanostructure to introduce the mismatch strain in shells and evaluated the reactivity of oxygen reduction reaction. And the core-shell mismatch strain has been drawn a great deal of attention in other experimental work [27].

Fischer-Tropsch synthesis (FTS), the conversion of syngas (CO and H<sub>2</sub>) into liquid fuels and high value-added chemicals, is a typical transition metal-catalyzed reaction. Iron-based catalysts employed as one of the most promising FTS catalysts have been studied extensively from preparation [28,29] to the optimization of reaction conditions [29,30]. However, to the best of our knowledge, the effect of strain on iron-based FTS catalyst has been rarely reported in the literature so far. There is quite some consensus that iron carbides are the actual active phase and prevailing at the surface of the catalysts [31,32]. However, it is not clear whether the metallic Fe is an active phase since it is easy to transform into iron carbides under syngas. Phase transformations and carbon deposition of the conventional iron catalysts during FTS process make the single strain study difficult. In order to minimize the impact of phase change, a kind of FeCrAl alloy wire with superior anti-oxidation, anti-carbidization and excellent thermal stability is selected as the object to study the strain induced reactivity. The wire catalyst has the advantage of simple mechanical strain introduction and facile characterization of strain.

Herein, we report a research on the relationship between the lattice strain and FTS activity over FeCrAl alloy wire catalyst. The different strain levels are obtained by exerting force, then annealing at various temperatures. A volcano plot is derived between strain and FTS activity. Appropriate strain promotes the catalyst to sweep through the activity peak. It is also demonstrated that such a strain dependent behavior is related to the variation in d-band electronic property of the metal.

## 2. Material and methods

### 2.1. Catalysts preparation

A kind of FeCrAl alloy wire (purchased from Shanghai Shuqing Electric Alloy Co., Ltd) with excellent anti-carbidization, anti-oxidation and excellent thermal stability was adopted as FTS catalyst to explore the strain induced reactivity. The nominal composition is 0Cr21Al6 and the balance Fe is about 73 wt%. The wire diameter is 0.2 mm. We exerted external stress on iron alloy wire and followed by annealing at 400 °C, 500 °C and 600 °C for 2 h in H<sub>2</sub> to obtain samples with different strain levels. The stress was carried out by a tension gauge, and then the wire was twisted to form a roll before putting it into the reactor.

### 2.2. Characterization

X-ray diffraction (XRD) spectra were obtained on a D/max-RA diffractometer with Cu K $\alpha$  radiation running at 30 mA and 40 kV. The XRD analysis was used to identify crystalline phase and calculate microstrain. Field emission scanning electron microscopy (FESEM) measurements equipped with an energy dispersive spectrometer (EDS) detector were carried out on the instrument JSM-7001F (Japan), which were used for surface morphology and chemical composition analysis. N<sub>2</sub>-adsorption isotherms were measured on a Tristar II3020 analyser at 77 K. X-ray photoelectron spectroscopy (XPS) measurements were carried out on the Thermo Scientific ESCALAB 250Xi equipment, which was employed to determine the surface composition and valence state of the surface elements. Vickers hardness of samples was measured using

SCT-150 digital micro hardness tester. The magnetic characterization was performed on a vibrating sample magnetometer (Lake Shore 7410 VSM) at room temperature. Magnetic field strength was set from -20 Oe to 20 Oe with the mass of 20 mg. CO-temperature programmed desorption (CO-TPD) experiments were operated on an own-manufactured reactor along with pulse injection. The exhaust behavior was recorded by a quadruple mass spectrometer that linked in outlet of the reactor. The temperature was heated up to 800 °C with the ramp of 15 °C/min.

### 2.3. FTS performance

The FTS performance of iron alloy wire was carried out in a fixed-bed reactor. A mass of 1.5 g catalyst was put in the flat-temperature zone of the reactor. All the catalysts were served in the reaction directly without activation procedure. FTS reaction conditions were designed at 345 °C, 20 bar, 0.2 g/(g·h) and the feed gas composition was H<sub>2</sub>/CO = 2. The condensable products were collected by a hot trap and a cold trap. The exit gas was periodically analyzed on line by three gas chromatographs with two thermal conductivity detectors (TCD) and a flame ionization detector (FID).

### 2.4. Theoretical calculations

We performed periodic density functional theory (DFT) calculations using the Vienna ab initio simulation package (VASP). The exchange correlation effects were described within the generalized gradient approximation using the Perdew-Burke-Ernzerh (PBE) functional. The ionic cores were represented by projector augmented wave potentials. For structure optimization, the plane-wave basis was expanded up to a cutoff energy of 400 eV and the mesh of k points was set at 5 × 5 × 1. For finely analysis of the d band center and transfer between s and d electrons, single point calculations were conducted with 500 eV cutoff energy and 9 × 9 × 1 k point mesh. The number of bands was increased to make sure that all relevant states above the Fermi level (E<sub>f</sub>) were included.

The lattice parameters of body centered cubic crystal of bulk FeCr alloy were adopted according to Ref. [33]. The 2 × 2 (1 1 0) surface unit cells were fabricated with 25% Cr atoms and 75% Fe atoms. All considered surfaces were modeled by a slab of five layers. The slabs were separated by 20 Å of vacuum to eliminate slab-slab interactions. The atoms at two bottom layers were fixed during the structure optimization.

We calculated the surface energy by increasing or decreasing the lattice parameters. The lattice parameters were changed with the same percentage in a and b directions, meanwhile the lattice of c direction was fixed. The lattice cell with the lowest surface energy is seen as the most stable surface without strain. It is evidenced that with lateral expansion and compression the surface energy increased similarly to parabolic curve.

## 3. Results and discussion

### 3.1. Lattice strain analysis and phase identification

The phase identification and microstrain estimation [34] were investigated through X-ray diffraction (XRD) line broadening, as shown in Fig. 1. The diffraction peaks appearing at 44.7°, 65.0°, 82.3° are attributed to the body centered cubic structure Fe (JCPDS No. 06-0696) [35]. It is noteworthy that the main phase composition is still metallic Fe after FTS reaction, albeit with the carbon species (2 $\theta$  = 26.3°) generate in the used catalysts, as displayed in Fig. 1b. This can be attributed to the superior anti-carbidization of FeCrAl alloy, resulting in the negligible iron carbides formation

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