



# Successive reduction-oxidation activity of FeO<sub>x</sub>/TiO<sub>2</sub> for dehydrogenation of ethane and subsequent CO<sub>2</sub> activation

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## ABSTRACT

Prototype FeO<sub>x</sub>/TiO<sub>2</sub> was applied for dehydrogenation of ethane to ethylene and successive CO<sub>2</sub> activation to CO for further chemical looping (CL) application. The Fe(5)/TiO<sub>2</sub> exhibited a facile redox cyclic activity with an insignificant coke formation and comparable CO<sub>2</sub> activation through reduction-oxidation reaction cycles. During the oxidative dehydrogenation of chemical looping (CL-ODH), the Fe nanoparticles (Fe<sub>2</sub>O<sub>3</sub>) on the rutile TiO<sub>2</sub> were partially transformed to the thermally stable FeTiO<sub>3</sub> phases with its lower oxidation state (Fe<sup>2+</sup>) below 700 °C. However, the formations of Fe<sub>2</sub>TiO<sub>5</sub> phases were found to be less active than the smaller sizes of iron oxides (Fe<sup>3+</sup>). The thermally stable iron phases with their reversible redox natures between FeTiO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> phases were responsible for a stable reduction-oxidation activity. The robust preservation of the partially reduced surface Fe<sup>2+</sup> sites with the copresence of the larger Fe<sub>2</sub>O<sub>3</sub> hematite crystallites on the TiO<sub>2</sub> was responsible for improving the redox activity and stability.

## 1. Introduction

A fast increase of anthropogenic CO<sub>2</sub> in an atmosphere has been mainly considered as a major chemical component for a recent global warming problem [1–3], and it largely encourages to develop effective utilization methods of CO<sub>2</sub> to value-added chemicals. Among the proposed chemical processes, one potential way to utilize CO<sub>2</sub> seems to be a chemical looping (CL) process, which is based on redox cycles of oxygen carriers such as partially reducible transition metal oxides [4–7]. The CL process for typical combustion reaction is generally composed of two interconnected reactors such as fuel reactor (reduction) and air reactor (oxidation) [8–10]. The oxygen carriers can release the active oxygen atoms from crystalline lattices in the fuel reactor through a reduction of metal oxides, and the partially reduced oxides can be regenerated by the oxidation reaction with air or CO<sub>2</sub> to simultaneously generate CO in an air reactor [11,12]. In terms of the CL scheme, the combination of CL with an oxidative dehydrogenation of light paraffins (CL-ODH) has a lot of potentials for a direct CO<sub>2</sub> capture/transformation as well as simultaneous light olefin production. For example, ethane (C<sub>2</sub>H<sub>6</sub>) dehydrogenation to ethylene (C<sub>2</sub>H<sub>4</sub>) can be carried out at a fuel reactor, whereas an air regenerator of the partially reduced metal oxides can be operated under CO<sub>2</sub> reduction to CO. One of the most important building blocks in petrochemical industries is ethylene, which is a starting material for the production of various

petrochemical intermediates [13,14]. Generally, the ethylene feedstock has been produced through conventional steam cracking and/or fluidized catalytic cracking reaction [15–17]. However, the pyrolysis processes have many drawbacks such as highly endothermic reaction natures requiring higher operation temperatures up to 1100 °C with substantial energy consumption by producing 1.0–1.2 ton(CO<sub>2</sub>)/ton (C<sub>2</sub>H<sub>4</sub>) with a large amount of coke depositions [18–20]. Although direct oxidative dehydrogenation (ODH) of paraffins have many potential advantages for olefin production, there are a number of unsolved critical challenges for its commercial implementation such as the requirement of air separation unit (ASU) and safety issues due to the copresence of oxygen and ethane with a comparable separation cost of the final gaseous products [21,22]. The proposed CL-ODH processes in the present study can be described with the following two main reaction steps;

- (1) Reduction step of metal oxides (fuel reactor):  $C_2H_6 + M_xO_y \rightarrow C_2H_4 + M_xO_{y-1} + H_2O$
- (2) Oxidation step of metal oxides (air reactor):  $CO_2 + M_xO_{y-1} \rightarrow CO + M_xO_y$

Compared to the general co-feeding of ethane and oxygen for ODH reaction, the CL-ODH by using the active lattice oxygens of the heterogeneous catalysts has been less studied. Several vanadium-based

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