Oxidative dehydrogenation of ethane and subsequent CO_2 activation on iron oxide-impregnated TiO_2 for chemical looping application

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Abstract:

Chemical looping process application for oxidative dehydrogenation (CL-ODH) of ethane was verified using iron oxide (Fe_2O_3)-impregnated on TiO_2 support to simultaneously produce the ethylene by ODH as well as CO by subsequent CO_2 activation on the reduced iron oxides. A higher selectivity to ethylene by ethane dehydrogenation and lower CO_2 activation to CO were observed on the 10wt%Fe/TiO_2, which has smaller crystallite sizes and less aggregation as confirmed by N_2-sorption, XRD, H_2-TPR, and XPS analysis.

Keywords: Chemical looping, Oxidative dehydrogenation (ethane), CO_2 activation, Fe/TiO_2, Redox cycle.

1. Introduction

Commercialized olefin productions have been based on the steam cracking of naphtha, alkanes, and so on[1], however some significant process problems such as coke deposition and CO_2 emissions have been required to be solved. As an alternative method for selective olefin production, oxidative dehydrogenation by chemical looping process (CL-ODH) on the reducible transition metal oxides has been proposed under an O_2-deficient conditions[2,3]. The CL-ODH reactions follows the reduction step of $C_2H_6 + MeO_x \rightarrow C_2H_4 + MeO_{x-1} + H_2O$, and subsequent oxidation step of $MeO_{x-1} + CO_2 \rightarrow CO + MeO_x$ through the redox cycles of meal oxides. The present study has been focused on investigating the Fe/TiO_2 as an efficient prototype catalyst for chemical looping application.

2. Experimental sections

The TiO_2 nanoparticles was previously synthesized by a soft-template method with structure-directing agent of hexadecyl-trimethylammonium bromide(CTAB). Titanium isopropoxide precursor was added slowly into the aqueous CTAB solution under stirring for 24 h at room temperature, and the mixtures were transferred into Teflon-lined stainless-steel autoclave kept at 110 °C for overnight. The as-prepared powder was washed thoroughly with deionized water and dried at 110 °C for 12 h and finally calcined at 400 °C for 1 h. The iron metal supported TiO_2 catalysts (Fe/TiO_2) were prepared by using iron nitrate precursor through impregnation method, which were calcined at 500°C for 6 h, and they were denoted as Fe(x)/TiO_2 with x = 5, 10, 15 and 20 wt%Fe. Catalytic activity was measured at ambient pressure in a fixed bed tubular reactor with 0.5 g of Fe/TiO_2 at temperature of 550 °C for 4 h using 20vol%C_2H_6/N_2 for a reduction reaction of iron oxides. The CO_2 activation to CO for oxidation reaction was carried out just after the reduction reaction after purging it under N_2 flow at 700 °C using 20vol%CO_2/N_2. The product gases for the separate redox reactions were analyzed using an on-line gas chromatography (Younglin, YL6000) equipped with a Carboxen 1000 packed column using thermal conductivity detector as well as a flame ionization detector with a Plot Q capillary column to analyze the hydrocarbons formed simultaneously.

3. Results and discussion

Figure 1 shows the characteristic bulk and surface properties of the fresh Fe/TiO_2, and N_2 adsorption-desorption analysis revealed a typical type IV isotherm with the decreased surface area of Fe/TiO_2 by increasing the concentration of iron oxides from 33.9 to 10.4 m^2/g with similar pore sizes as shown in **Table 1**. XPS spectra of $2p_{3/2}$ peak appeared at ~ 712 eV can be attributed to the Fe^{3+} species from the main phases of hematite (α-Fe_2O_3), which was confirmed by XRD patterns of the fresh Fe/TiO_2 with the anatase TiO_2

phases (**Figure (D-1**). The reducibility of iron oxides on Fe/TiO_2 measured by TPR showed two characteristic peaks below 400 ^{o}C and ~ 570 ^{o}C for the reduction of $Fe_2O_3(Fe^{3+})$ to $FeO(Fe^{2+})$ and its subsequent reduction to metallic Fe^0, respectively (higher reduction peak above 700 ^{o}C from the partial reduction of anatase TiO_2 phase). As shown in XRD patterns (**Figure 1(D-2)** and **(D-3)**), the original hematite phases were reduced to Fe_3O_4 and metallic iron on the reduced Fe/TiO_2 and the main iron phases after redox reaction were Fe_3O_4 phases, which were thermodynamically stable iron phases. The catalytic activity as summarized in **Table 1** revealed a higher selectivity to ethylene by ethane dehydrogenation (95.7%) and lower CO_2 activation to CO (0.12 mmol/g_{cat}) on the 10wt%Fe/TiO_2, which was attributed to the smaller iron crystallite sizes with less aggregations during redox reaction as confirmed by the surface I_{Fe}/I_{Ti} ratio from the XPS analysis on the fresh and used Fe/TiO_2 catalysts.

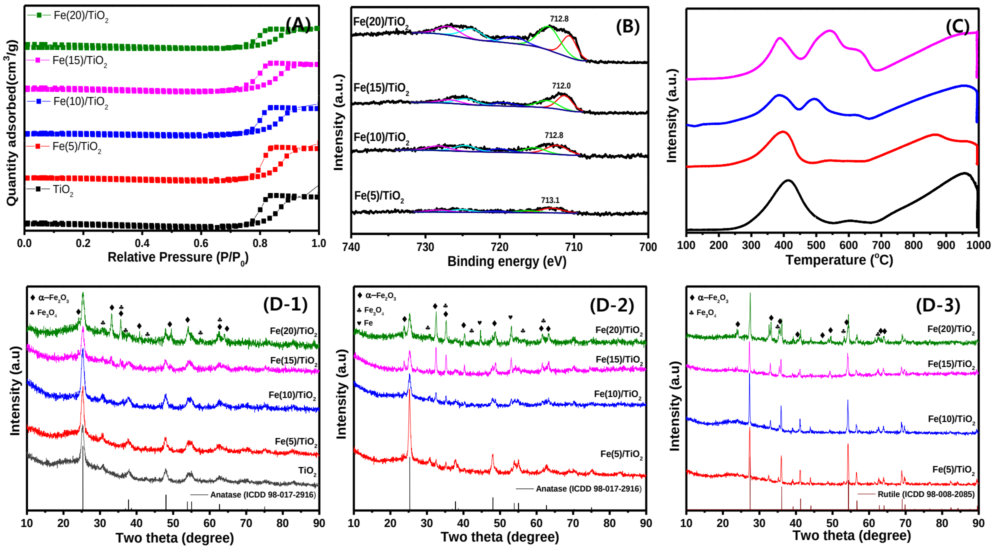

Figure 1. Bulk and surface properties of the fresh Fe/TiO_2; (A) N_2-sorption, (B) XPS, (C) TPR and (D) XRD analysis for (1) fresh, (2) reduced at 550 ^{o}C and (3) used Fe/TiO_2 after redox reaction

Table 1. Physicochemical bulk and surface properties of the Fe/TiO_2 with its catalytic activity

Catalyst	N_2-sorption[a]	XRD (fresh/used)	H_2-TPR	XPS (eV) (fresh/used)		Catalytic activity (redox, mol%)		
	S_g /P_v /P_d	Crystallite size (Anatase /Rutile, nm)	Consumed amount of H_2 (mmol/g_{cat})	Fe $2p_{3/2}$	I_{Fe}/I_{Ti}	Conversion of C_2H_6 (reduction)	Product distributions by reduction of Fe_2O_3 ($CO/CO_2/CH_4/C_2H_4$)	CO by oxidation (mmol/g_{cat})
Fe(20)/TiO_2	10.4/0.09/8.6	9.5/39.0	1.99	712.8/711.5	5.67/0.89	3.9	10.2/1.4/3.2/85.2	0.59
Fe(15)/TiO_2	25.5/0.14/8.2	9.3/35.4	1.17	712.0/711.5	0.38/0.89	4.3	2.8/0.5/2.9/93.7	0.19
Fe(10)/TiO_2	31.4/0.14/8.8	9.1/40.8	1.61	712.8/711.3	0.20/0.44	6.2	0.6/0.3/3.4/95.7	0.12
Fe(5)/TiO_2	33.9/0.17/9.2	9.6/12.4	2.40	713.1/709.8	0.08/0.25	9.8	3.8/1.5/5.4/89.1	0.33

[a] S_g, P_v, and P_d represents the specific surface area (m^2/g), pore volume (cm^3/g) and average pore diameter (nm), respectively.

4. Conclusions

The prototype Fe/TiO_2 catalyst with main hematite (Fe_2O_3 phases was investigated for the redox reaction of ODH of ethane and CO_2 activation, and a higher selectivity to ethylene by ethane dehydrogenation (95.7%) on the 10wt%Fe/TiO_2 was observed due to its smaller iron crystallite sizes with less aggregations during the redox reaction (CL-ODH) by maintaining thermodynamically stable magnetite (Fe_3O_4) phases, which can be applied for the further chemical looping process.

References

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