Oxidative Dehydrogenation of Ethane with CO_2 over CrO_x Catalysts Supported on Al_2O_3 modified by ZrO_2 and/or CeO_2

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Abstract: A series of Cr-containing catalysts (with Cr content corresponding to one theoretical monolayer) supported on Al_2O_3, ZrO_2/Al_2O_3, CeO_2/Al_2O_3 and $Ce_xZr_{(1-x)}O_2/Al_2O_3$ was prepared using the impregnation techniques. The catalysts are characterized by the low-temperature N_2 sorption, XRD, TPR, UV-vis spectroscopy and tested in oxidative dehydrogenation of ethane using CO_2 as an oxidant. The results of physical-chemical characterization show that chromium is located on the support surface in amorphous Cr(VI) state. The addition of ZrO_2 and/or CeO_2 to the alumina support leads to increased activity in both the direct and the oxidative dehydrogenation reactions.

Keywords: oxidative dehydrogenation, ethane, carbon dioxide as an oxidant, chromia

1. Introduction

Ethylene, propylene and isobutylene are important building blocks in organic and polymeric synthesis in chemical and petrochemical industry. A growing demand in olefins requires new technologies in addition to traditional steam and catalytic cracking methods of olefin production. Catalytic dehydrogenation of alkanes is one of the most promising ways to obtain olefins among the new alternative routes due to high purity of the produced olefin. However, thermodynamic limitations make it difficult to carry out the direct dehydrogenation of ethane with high yield and selectivity towards ethylene. To avoid such limitations and shift the equilibrium towards the formation of target products, the oxidative dehydrogenation (ODH) of ethane is proposed by several scientific groups[1,2]. Oxygen or carbon dioxide are used as oxidants. The prospects of using CO_2 as a mild oxidant are caused by the absence of deep oxidation, high selectivity to target olefin and utilization of CO_2 as a resource.

The reaction pathway in ODH using CO_2 is known to depend strongly on the support nature[2]. According to our previous results[3], Cr-containing catalysts supported on γ-Al_2O_3 and ZrO_2 showed the highest rates of C_2H_4 formation ($mmol\cdot h^{-1}\cdot g^{-1}$) via ODH-$CO_2$ of ethane in comparison with those over CrO_x/CeO_2 and $CrO_x/Ce_xZr_{1-x}O_2$ samples. Taking into account the range of products and their stoichiometry[4], the following reactions set was proposed:

selective ODH: $C_2H_6 + CO_2 \leftrightarrow C_2H_4 + CO + H_2O$	water–gas shift reaction (RWGS): $CO_2 + H_2 \leftrightarrow CO + H_2O$
direct dehydrogenation: $C_2H_6 \leftrightarrow C_2H_4 + H_2$	cracking: $C_2H_6 + H_2 \leftrightarrow 2CH_4$
non-selective reaction: $C_2H_6 + 5CO_2 \leftrightarrow 7CO + 3H_2O$	dry reforming: $C_2H_6 + 2CO_2 \leftrightarrow 4CO + 3H_2$

However, for CrO_x/Al_2O_3 catalyst the process consisted of two main reactions: direct dehydrogenation and RWGS, while for CrO_x/ZrO_2 sample ethylene was mainly formed through selective ODH. CrO_x/CeO_2 and $CrO_x/Ce_xZr_{1-x}O_2$ catalysts were characterized by lower ethylene formation rate due to high contribution of non-selective reactions of ethane transformation along with selective ODH. Thus, the combination of support properties can be used to design effective catalysts for ethane ODH with CO_2.

The purpose of the present work is to study the effect of ZrO_2 and/or CeO_2 addition on the state of the active component in CrO_x/Al_2O_3 catalysts and its activity in ODH-CO_2 of ethane.

2. Experimental

Initial γ-Al_2O_3 support was obtained by thermal decomposition of AlO(OH). ZrO_2 and/or CeO_2 modified γ-Al_2O_3 supports were prepared by incipient wetness impregnation technique using water solutions of $ZrO(NO_3)_2\cdot 2H_2O$ and/or $Ce(NO_3)_3\cdot 6H_2O$ stabilized by citric acid with ZrO_2 and/or CeO_2 contents of 2.5 $at_{Zr(Ce)}/nm^2$. The supports were dried at 80 °C overnight and calcined at 600 °C for 4 h. Cr-containing catalysts with Cr loading corresponding to a monolayer (5 at_{Cr}/nm^2) were prepared by incipient wetness impregnation of γ-Al_2O_3, ZrO_2/Al_2O_3, CeO_2/Al_2O_3 and $Ce_xZr_{(1-x)}O_2/Al_2O_3$ using aqueous solution of H_2CrO_4. The catalysts were dried at room temperature for 12 h and calcined at 600 °C for 4 h. The supports and catalysts were characterized by low-temperature N_2 sorption, XRD, TPR, UV-vis spectroscopy and tested in a fixed-bed reactor in oxidative dehydrogenation of ethane with CO_2 between 500 and 700 ºC in consecutive incremental steps of 50ºC.

3. Results and discussion

The study of the porous structure showed that all samples were mesoporous and the specific surface areas varied in the ranges of 146-201 and 132-159 m^2/g for supports and catalysts, respectively. The absence of reflexes of Cr-containing phases in XRD patterns for all catalysts indicates highly dispersed state of CrO_x on the surface of the supports. However, the reflexes of cubic phases of ceria and mixed cerium–zirconium oxides were found for catalysts modified by CeO_2 and $Ce_xZr_{1-x}O_2$. The DRS results indicated formation of Cr^{VI} state, the adsorption bands of Cr^{III} were not observed. It was shown by TPR-H_2 that the addition of ZrO_2 and/or CeO_2 influenced on the reducibility of Cr^{VI}.

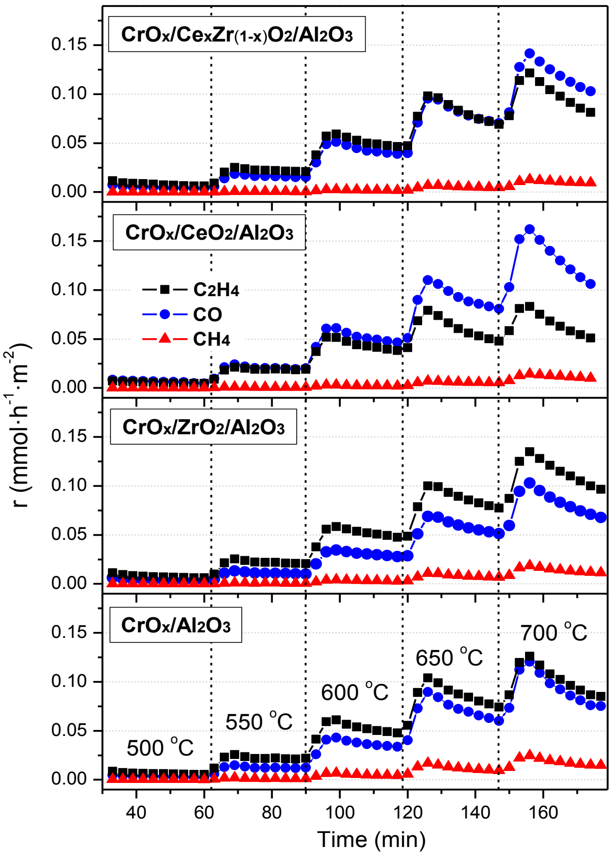

Figure 1. Specific rates of formation of ethylene, methane and CO in ODH-CO_2 of ethane over Cr-containing catalysts.

The specific formation rates of C_2H_4, CO and CH_4 during the ODH-CO_2 for all catalysts are shown in Figure 1. Modification of the support of CrO_x/Al_2O_3 catalyst leads to changing of C_2H_4/CO ratio and decreasing of amount of by-products (CH_4 and coke). The $CrO_x/ZrO_2/Al_2O_3$ catalyst showed the highest activity in ODH-CO_2 of ethane. Addition of ZrO_2 caused the increase of ethylene formation rate and the decrease of that of CO as compared to unmodified CrO_x/Al_2O_3. The highest formation rate of CO and the lowest one of C_2H_4 are observed for CeO_2-modified catalyst. The modification by $Ce_xZr_{(1-x)}O_2$ did not lead to changing of ethylene formation rate. The addition of ZrO_2 and/or CeO_2 also leads to decrease of coke deposition on the catalyst surface.

4. Conclusions

All the studied catalysts mainly contain chromium in the Cr^{VI} state. The direct DH of ethane and RWGS is the main route over CrO_x/Al_2O_3, with cracking and coke formation as side reactions. Addition of ZrO_2 and/or CeO_2 to CrO_x/Al_2O_3 catalyst results in selective ODH. For $CrO_x/ZrO_2/Al_2O_3$ catalyst, ethylene is additionally formed by selective ODH-CO_2 reaction, while non-selective and/or dry reforming reactions take place on $CrO_x/CeO_2/Al_2O_3$ catalyst as shown by the higher CO formation rate. These changes in the main reactions can be ascribed to the differences in the chromium reducibility caused by its interaction with the support.

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