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Oxidative dehydrogenation of propane over catalysts based on carbon nanofibers

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Abstract

Carbon nanofibers (CNF) and CNF-supported phosphoric oxides were tested as the catalysts for oxidative dehydrogenation of propane (ODP). The catalysts were characterized by SEM, TEM, X-ray diffraction (XRD), N_2 adsorption and temperature-programmed surface reaction (TPSR). CNF itself is an effective catalyst for ODP, but the high propene yield can only be achieved at high reaction temperature, which would cause CNF gasification. CNF-supported phosphoric oxides can operate at 500 °C without gasification and a 39.63% propene selectivity could be reached at a 42.07% propane conversion. Carbonyl-like groups on the CNF surface could be the active sites for ODP.
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Keywords: Oxidative dehydrogenation; Propane; Carbon nanofiber

1. Introduction

The wide availability and low price of light alkanes and the fact that they are generally environmentally non-aggressive products have provided incentives for their use as raw materials in the chemical industry [1,2]. Investigations on the catalytic oxidative dehydrogenation of propane (ODP) have been undertaken since this route is expected to lead lower costs of propylene production as compared with the non-catalytic and non-oxidative processes [3,4]. Oxidative dehydrogenation (ODH) also could be a conceptually interesting route as limitations by the chemical equilibrium are removed by coupling of dehydrogenation and hydrogen oxidation. Moreover, the presence of oxygen limits coking and extends, therefore, catalysts lifetimes [1,3,5]. Vanadium and molybdenum oxides usually are the main elements present in catalysts used for ODP [2–4,6].

As a new kind of carbon materials, carbon nanofilaments (tubes and fibers) have been intensively studied [7–11]. Until now far less work has been devoted to the catalytic application of carbon nanofilaments [8]. When most of the problems related to the synthesis of large amounts of these nanostructures are solved or almost solved, a large field of research is open to these materials with fascinating characteristics [8–11]. As for ODH, Schlögl and co-workers studied catalytic performances of multi-walled nanotube and onion-like carbon for ethylbenzene oxidative dehydrogenation (ODE), where styrene selectivity of 68% allowed high styrene yields of 62% [12,13]. These results show that carbon nanofilaments have great opportunities for ODH and encourage us to explore the use of carbon nanofibers (CNF) as catalysts for ODP.

2. Experimental

2.1. Catalysts preparation

The CNF sample was produced by decomposition of CO over a γ-Al_2O_3 supported 20 wt% nickel–iron alloy catalyst. Details of the procedure were described in the reference [14]. Briefly, the catalyst was reduced in a 25 vol% H_2/Ar mixture (total flow rate 160 ml/min) for 3.0 h at 600 °C. Then the

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reactant gas, 80 vol% CO/H_2 mixtures (total flow rate, 100 ml/min), was allowed to flow over the catalyst for a period of up to 24 h. The yield of CNF was about 20 g/g_{cat}. To remove metallic inclusions, the CNF was repeated washed in 2 mol/l HCl over a period of 7 days. Then, the CNF sample was filtered, washed by a large amount of deionized water until the pH of filtrate was close to 7 and dried at 120 °C overnight. Before test as catalysts for ODP, the CNF was calcined in air at 500 °C for 2 h and designated as CNF1 hereafter.

Before phosphoric oxide was supported, the CNF was immersed in concentrated HNO_3 for 7 days. The supported catalysts were prepared by incipient-wetness impregnation method using $(NH_4)_2HPO_4$ aqueous solution as phosphorus resource. The loading is 5wt%, which is calculated by weight of P_2O_5. After impregnation and drying, the samples were calcined in argon at 800 °C for 2 h and in air at 600 °C for 2 h. This catalyst are called 5P1/CNF for short. During the process of calcinations in air, the two samples have weight loss of 16.8 and 7.6 wt%, respectively.

2.2. Catalysts characterization

Structures of the CNFs were characterized by SEM (JOEL JSM3360LV, Japan) and HRTEM (JOEL JSM2010, Japan). The textural properties had been obtained from N_2 adsorption–desorption isotherms (ASAP 2010, Micromeritics, USA) at −196 °C after out-gassing the samples at 190 °C and 1 mmHg for 6 h. X-ray diffraction (XRD) was performed on a Rigaku D/Max2550VB/PC (Rigaku, Japan, Cu Kα radiation).

Temperature-programmed desorption (TPD) was used to determine categories and amounts of surface oxygen complexes on CNF1. The TPD spectra were obtained by heating the samples in Ar. The temperature program was as follows: 1 h at 150 °C and 10 °C/min ramp rate to 650 °C; 30 °C/min to 150 °C; 10 °C/min to 1000 °C. The temperature-programmed surface reaction (TPSR) of propane was performed to explore the role of CNF surface oxygen complexes in catalyzing ODP. The samples were TPD in Ar to 650 °C, cooled in Ar to 150 °C, and then the sample temperature was raised at a constant ramping rate of 10 °C/min in a gas mixture of 8 vol% C_3H_8/Ar (total flow rate, 50 ml/min). At a certain temperature, the gas may react in the presence of samples, creating products. TPD and TPSR runs were carried out on Autochem II 2920 (Micromeritics, USA). The outgoing gas was diverted to a quadrupole mass spectrometer (Questor, ABB Extrel, USA) to be analyzed. Concentrations of Ar, C_3H_8, C_3H_6, C_2H_4, CH_4, CO_2 and CO were calculated by the signal intensities of mass 40, 39, 41, 27, 16, 44 and 28, respectively. No C1–C2 hydrocarbon is detected by QMS.

2.3. Catalytic reaction

Catalytic experiments were performed at 1 atm pressure in a conventional fixed bed flow reactor made of stainless steel. The CNF catalysts were charged (particle size <0.18 mm) without inert diluents and were placed on quartz wool in the isothermal zone of the reactor. The free volume of the reactor was packed with silica and quartz wool. Under the experimental conditions used in this work, the homogeneous reaction could be neglected. If not specified in the article, the feed was composed of 4 vol% propane, 8 vol% oxygen and balance Ar. Analyses of reactants and products were carried out by using two separate on-line gas chromatographs (Agilent 4890D) with TCD detectors, using a HP-Plot Q capillary column (30 m × 0.53 mm) for hydrocarbons and a TDX packed column (2 m) for permanent gases. The tail gas was diverted to a container filled with cyclohexane in order to collect possible organic oxygenates produced in the catalytic experiments. The solution was analyzed by GC–MS (Micromass GCT, GB), which was equipped with a DB-5 ms column. The gases used in catalytic experiments, oxygen (99.999%), propane (99.5%) and argon (99.99%), were obtained from Shanghai Rex Co-Perfect Instrument Co., Ltd. and used without further purification.

3. Results and discussions

3.1. Catalyst structure

The SEM picture (Fig. 1(a)) shows that the CNF has an even diameter which is estimated of 30–40 nm. TEM image (Fig. 1(b)) reveals that the CNF has a hollow core, and its graphene layers are about 15–20° inclining to the axis. Fig. 2 shows the XRD patterns. The (0 0 2), (1 0), (0 0 4) and (1 1 0) graphite peaks are observed. The interplanar distance d_{002} and crystallite height, L_c, are presented in Table 1. The d_{002} is a little higher than ideal graphite (0.335 nm). But the parameters of different samples are close, which indicates that the catalyst structures are not affected much after the preparation processes and catalytic experiments. No metal and their oxides diffraction peak is found, which implies the metal is removed from the CNF. No phosphoric oxides diffraction peak is found either. That is because the phosphoric oxides are amorphous. The textural properties are listed in Table 1. All the samples have small micropore volumes. The BET area is reduced after supporting phosphoric oxides, which implies that phosphoric oxides occupy part of the CNF surface. After testing 5P1/CNF as catalyst for ODP at 500 °C for 6 h, the textural properties are similar to the original samples.

3.2. TPD results

The TPD spectrum of CNF1 is presented in Fig. 3. TPD can provide a good overview of the sample's surface properties [15–17]. According to the desorption products and desorption peak temperature (T_m), the amount and categories of CNF surface oxygen complexes could be

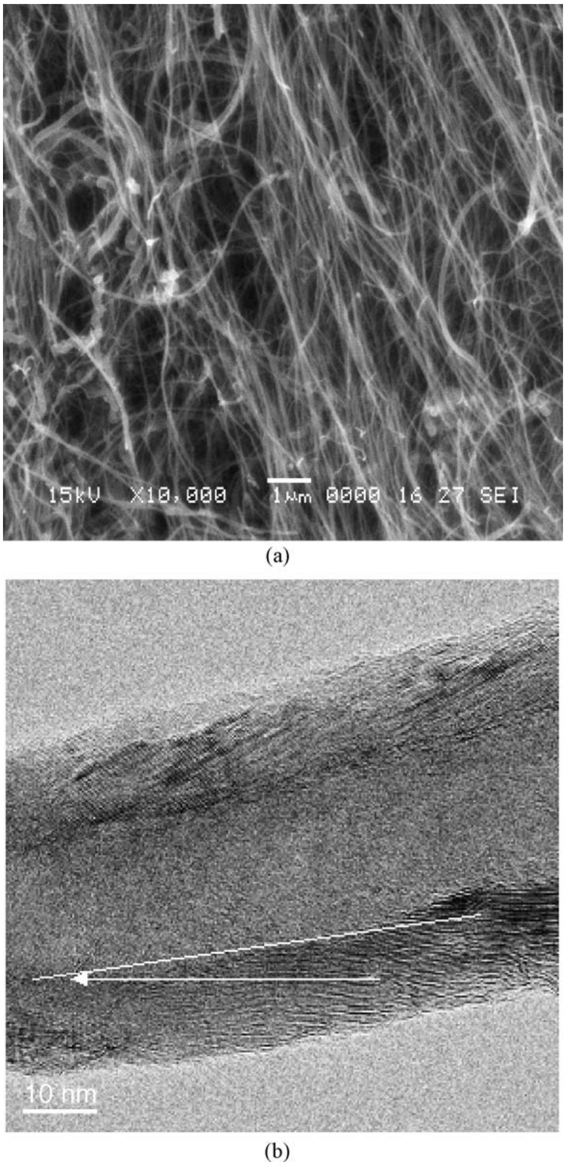

Fig. 1. SEM (a) and TEM (b) image of the CNF.

determined. The method has been summarized recently by Szymański et al. [16] and Figueiredo et al. [17]. After TPD up to 650 °C, no CO_2 but 0.90 mmol/g CO is desorbed from CNF1 surface in the successive TPD run up to 1000 °C. Two CO desorption peaks could be found centered at 800 and 950 °C, which can be assigned to carbonyl-like groups and basic oxides according to references [15–17]. The structure of basic oxides on carbonaceous materials is not unambiguous, but it always contains a C=O bond. When

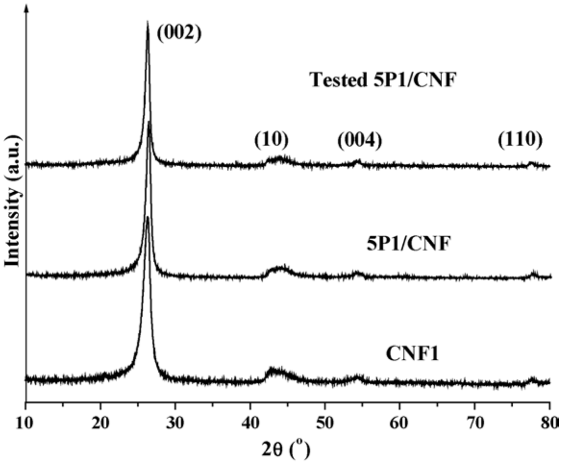

Fig. 2. XRD profiles of CNF catalysts.

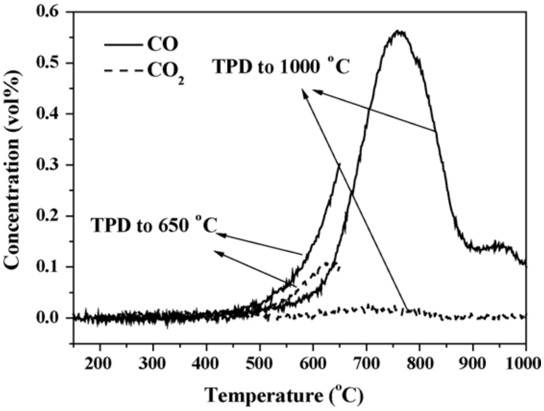

Fig. 3. Temperature-programmed desorption spectra of CNF1; carrier gas, Ar.

carbonaceous materials are oxidized in air, oxygen is easily combined with surface active sites, e.g. edge of the graphene layer and/or defect sites, to form these groups [15].

Comparing of the weight loss of the two catalysts during the calcinations process, it's easily to see the inhibition effect of phosphoric oxide on CNF oxidation. The function of phosphoric oxides have long been known [18,19]. Phosphorus can block active sites by forming either C–O–P or C–P–O at graphene edges [18,19], which decreases the availability of the sites where oxidation takes place. That also implies that the amount of surface oxygen complexes decreased after loading phosphoric oxides to CNF surface.

Table 1
Structure properties of the CNF catalysts

Sample	BET area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	d_{002} (nm)	L_c (nm)
CNF1	173.4	0.53	0.006	0.340	8.8
5P1/CNF	127.9	0.45	0.004	0.338	9.6
Tested 5P1/CNF[a]	136.8	0.49	0.006	0.338	9.0

[a] 5P1/CNF after tested as catalyst for ODP at 500 °C for 6 h; feed rate, $Ar/O_2/C_3H_8$=88:8:4 ml/min.

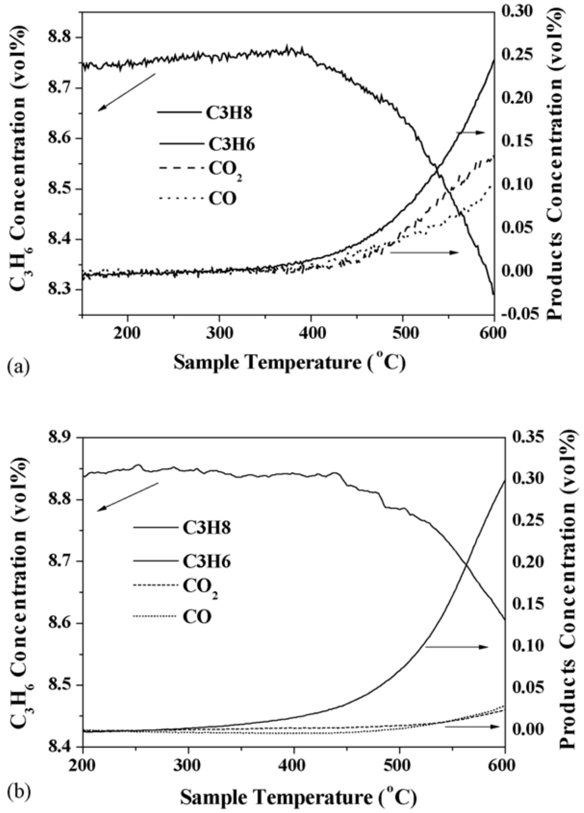

Fig. 4. TPSR of C_3H_8 over (a) CNF1, 0.1860g and (b) 5P1/CNF1, 0.1515g.

3.3. TPSR results

TPSR results are presented in Fig. 4. Propene is produced when the sample temperature is above 350 °C on both samples, which means converting of propane over CNF catalysts could occur in anaerobic condition. The desorption amount is 0.35 and 0.29 mmol/g for CNF1 and 5P1/CNF1, respectively, while the percentage of propene in the desorption substances over these two samples are 51.4 and 87.7%, respectively.

It's worth pointing out that no products (propene and CO_x) is detected by QMS in TPSR runs under the following circumstances: (1) TPD of CNF1 to 1000 °C, then cooled it down to 150 °C in Ar before the TPSR runs; (2) 5P1/CNF without calcinations in air and (3) no CNF sample is presented. Based on these results we can deduce that conversion of propane over CNF occurred on their surface oxygen complexes containing C=O bonds (carbonyl and basic oxides). These structures are also thought to be responsible for catalytic redox reaction on carbon surface [20–22].

3.4. Catalytic performances

GC analysis results show the main products of the reaction are propene, CO_2 and CO. Trace amount of degradation products, mainly ethylene, are also produced over 5P1/CNF at 500 °C. No organic oxygenate is detected by GC–MS.

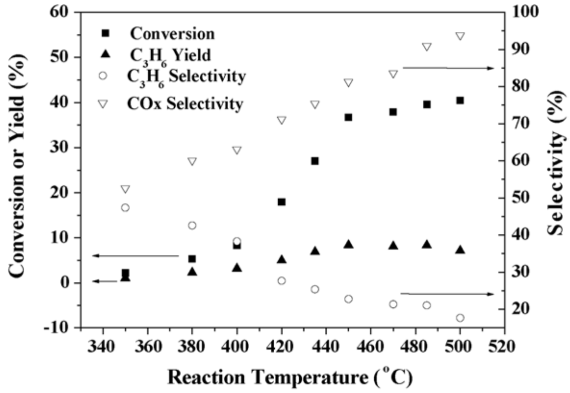

Fig. 5. Initial catalytic performances of CNF1; catalyst loading, 0.40g; feed rate, Ar:O_2:C_3H_8=88:8:4 ml/min.

The initial catalytic performances over CNF1 at different reaction temperatures are shown in Fig. 5. It is found that CNF1 is an effective catalyst for ODP: a 42.60% propene selectivity at a 5.33% propane conversion is achieved at 400 °C. Raising the reaction temperature leads to an increase of the propane conversion and propene yield. But the carbon balance is apparently above 105%, which means CNF gasification occurs, when the reaction temperature is over 450 °C.

Propene selectivity as a function of propane conversion is studied on CNF1 under different reaction conditions. The results are shown in Fig. 6. The C_3H_6 selectivity decreases with the increase of C_3H_8 conversion, which implies consecutive reaction of C_3H_6 degradation. Apparently, a high reaction temperature and O_2/C_3H_8 ratio is favored for high propene yield. Extrapolation the results shown in Fig. 6 to zero conversion show that the theoretical propene selectivity of ODP on CNF1 increases when the reaction temperature is raised. But the theoretical propene selectivity does not exceed 80% on this sample. Except that propane undergoes oxidative dehydrogenation to form propene and combustion of propane and propene to form CO_x, CNF gasification should be considered. As mentioned above, high propene yield and theoretical selectivity could be achieved at

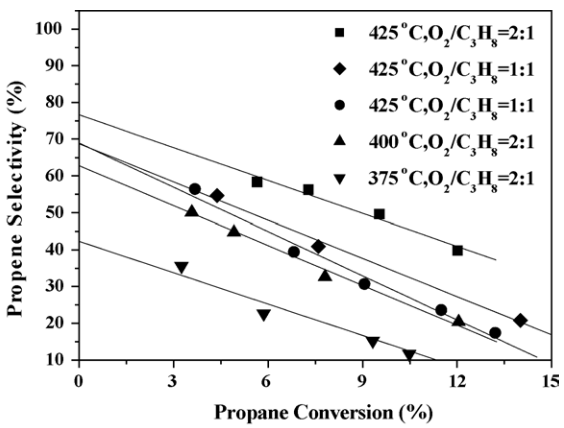

Fig. 6. Propene selectivity as a function of propane conversion over CNF1.

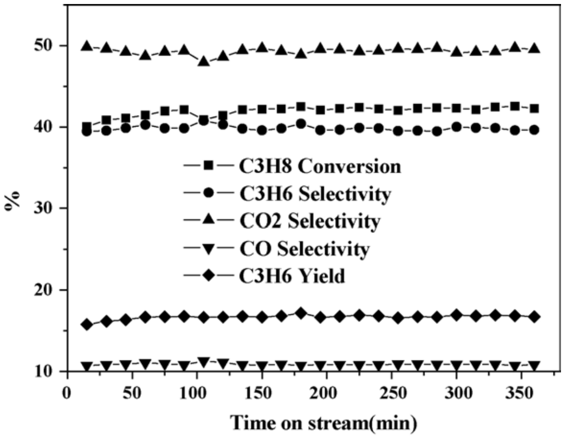

Fig. 7. Catalytic performances as a function of run length over 5P1/CNF.

high reaction temperature and O_2/C_3H_8 ration. But high reaction temperature and O_2/C_3H_8 ration is also benefit for CNF gasification, which limits achieve higher propene yields on CNF catalysts.

After introducing phosphoric oxides to the CNF, it's found that the catalytic activity decreases. For instance, the propene conversion is 36.70% over CNF1 while it's 17.64% over 5P1/CNF (450 °C; contact time $W/F = 37.3\ g_{cat}\ h\ (mol\ C_3H_8)^{-1}$). No apparent CNF gasification occurs under 525 °C. Evolution of catalytic performances with time for 5P1/CNF is presented in Fig. 7. The propane conversion and propene selectivity increases at the first hour on stream. Then a steady state is reached. Averaging the experimental points, a 39.63% propene selective is achieved at a 42.07% propane conversion over 5P1/CNF. It's worth noting that 5P1/CNF without calcination in air has a very low catalytic activity (0.56% at 500 °C), which testifies that the active sites for ODP, carbonyl-like groups, are introduced on the CNF by air oxidation.

Extrapolating the curve of propene selectivity as a function of propane conversion (the results are not shown) to zero results in a 95% theoretical propene selectivity. So, the phosphoric oxides on CNF surface can inhibit propane over-oxidative reactions, which is also testified by TPSR characterization.

4. Conclusions

CNF could be an effective catalyst for ODP when the gasification reaction is inhibited. Phosphoric oxides could tailor the density of surface oxygen complexes on CNF surface, which are active sites for ODP and CNF gasification. That enables CNF can operate at 500 °C without gasification and inhibit propane over-oxidation. A 39.63% propene selectivity could finally be reached at a 42.07% propane conversion over CNF-supported 5 wt% phosphoric oxides catalysts.

Acknowledgements

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