Study on Properties of Co-S-1 Zeolite and its Performance in Chemical Looping Oxidative Dehydrogenation of Propane

Ziyang Liu, Peng Bai[a*], Zifeng Yan[b*]

State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao, 266580, China

`zy-sio2@163.com,`[a*]`20080066@upc.edu.cn,`[b*]`19940001@upc.edu.cn`

Abstract. Propylene is an important industrial basic material, and propane dehydrogenation is an important industrial process for producing propylene. Compared with the current industrial process of direct dehydrogenation of propane. Oxidative dehydrogenation can generate heat for the reaction through direct oxidation of generated H2, significantly reducing the process energy consumption, and because of the consumption of H2, it can impact the reaction equilibrium and improve the conversion. In various processes of oxidative dehydrogenation, chemical looping oxidative propane dehydrogenation provide oxygen atoms through solid oxygen carrier. Due to the generated propylene will not be oxidized to COx, so it can obtain the highest selectivity of propylene, is the most promising method of propane dehydrogenation.

In this research, a supported oxygen carrier compound was prepared using industrial alumina carrier, and its oxygen carrying performance was characterized. In addition, two different Co-S-1 catalysts containing Co on S-1 zeolite were prepared by in-situ synthesis and impregnation methods, which show stable propane dehydrogenation performance. Their physical properties were characterized by XRD, BET, IR, SEM, and comparative analysis. Using a fixed bed reactor, both Co-S-1 catalysts alone and mixing with oxygen carrier was loaded into the catalyst bed, to carry out propane dehydrogenation catalytic reaction. Co-S-1 showed high catalytic activity, and the catalytic activity is improved after coupling with oxygen carrier. Co-S-1 prepared by impregnation method has similar propane dehydrogenation activity to Co-S-1 synthesized in situ, and can be coupled with oxygen carriers prepared by industrial carriers to improve catalytic conversion activity, and has high industrial application potential.

Keywords: S-1 zeolite, Oxidative Propane Dehydrogenation, Chemical Looping

1   Introduction

Propane dehydrogenation is an important propylene production process, and its production capacity has increased rapidly in recent years, so its related research has become a hot spot [1, 2]. At present, the main industrial applications are Olflex process

using a moving bed reactor with Pt-based catalyst, and CATOFIN process using a fixed bed reactor with uses CrOx-based catalysts. Reducing the production cost of propane dehydrogenation process will help improve its commercial competitiveness, so it is the main goal pursued by researchers. The production cost is mainly derived from raw material consumption and energy consumption, among which the separation of propane and propylene in the reaction product consumes huge energy.

Therefore, by consuming the hydrogen generated by the reaction, the reaction can be pulled forward to improve the one-way conversion rate. If the one-way conversion rate can be increased, the energy consumption of separating propane and propylene products can be reduced. At the same time, propane dehydrogenation is a strong endothermic reaction, and the reaction heat is also a huge part for energy consumption. Oxidative dehydrogenation can use generated H2 through oxidation directly heating the reaction, thus reduce the reaction heat consumption, and greatly benefits the economic efficiency of propane dehydrogenation process. In contrast with direct dehydrogenation, oxidative dehydrogenation involves oxygen to convert H2 generated.

Hence, some researchers have proposed a method to promote the dehydrogenation of propane, that is, the use of oxides that can be reduced as auxiliary catalysts[3-6].In this way, in the reaction process, the lattice oxygen of the oxide can be used to consume the H2 generated by dehydrogenation to generate water, and the heat released by this reaction process is directly coupled with the heat of the dehydrogenation reaction, and direct heating is used in the reaction process to achieve the most efficient use of energy. At the same time, due to the consumption of hydrogen in the reaction system, the propane dehydrogenation reaction can be pulled forward to achieve a one-way conversion rate higher than the general equilibrium conversion rate. This is called chemical looping oxidative dehydrogenation. It is characterized by the lattice oxygen from the solid oxide, which will be consumed with the continuous reaction, the oxygen carrier needs to introduce air regeneration through circulation, and the step cycle of dehydrogenation-purging - oxidation regeneration-purging needs to be repeated constantly to achieve the reaction of propane dehydrogenation from the process. This is similar to the CATOFIN process in terms of process flow and reduces one reduction step. It has a high research prospect.

This is different from oxidative dehydrogenation reactions using O2 or CO2 as oxidants, in which COx does not affect the selectivity of the reaction and potential separation problems [7]. However, most of researchers focus on the developing a bifunctional catalyst that can both provide dehydrogenation site and lattice oxygen, which showed high activity but very hard to balance the two functions [8]. Therefore, the modified zeolite with metal encapsulation is used as the catalyst, and the oxygen body is loaded separately, which can realize the chemical looping of oxidative dehydrogenation, and the oxygen content of the oxygen carrier can be flexibly adjusted. It can play the role of oxygen carrier to provide oxygen and consume hydrogen to achieve the coupling of propane dehydrogenation [9-10].

So, this research is focus on oxidative dehydrogenation process, and use solid oxidates as oxygen supplier to form a chemical looping process, its unique point lies in oxygen carrier and catalytic functions are provided by two separated materials. The oxygen carrier containing copper oxide was prepared by impregnation with industrial

common alumina carrier, and Co-S-1 catalyst was synthesized by two different methods, respectively by in-situ synthesis and post-synthesis impregnation. Co atom was introduced into S-1 zeolite, and its crystal structure, pore structure and morphology were and characterized and analyzed. The activity of propane dehydrogenation was evaluated, and it was found that the conversion rate of propane dehydrogenation was increased in the condition of cooperating with oxygen carrier.

2   Experimental

2.1   Catalyst Preparation

Cobalt nitrate (Co(NO3)2·6H2O, 99%), Ethanediamine (EDA, 99%), Tetraethyl Orthosilicate (TEOS, 98%), and Isopropanol (IPA, 99%), Tetrapropylammonium hydroxide solution (TPAOH, 25%) were obtained from Guoyao Chemical Reagent Co. All the chemicals are obtained as received without further purification.

The preparation of In situ Co-S-1(IS-Co-S-1): Insitu synthesis of Co-S-1 within was realized by a hydrothermal method. Firstly, calculated Co(NO3)2·6H2O and EDA (molar ratio of Co:EDA = 1:2.5) were added into deionized water and TPAOH. Then, TEOS was added to the above solution and stirred in an ice bath for 3 hr. The resultant solution was heated to 75 ℃ and stirred for 4 hr. After cooling down to room temperature, IPA was dropped into the above solution and stirred for 2.5hr. The molar ratio of the final gel was 1SiO2:xCoO:2xEDA:0.4TPAOH:4IPA:32H2O(0 < x < 0.05). The obtained mixture was put into a Teflon-lined autoclave at 155 ℃for 84 hr. The resulting sample was collected and washed with deionized water several times, dried at 110 ℃ overnight, and subsequently calcined in a muffle furnace at 550 ℃ for 4hr with a heating ramp of 2 ℃ min^{-1}. S-1 zeolite was synthesized with no Co(NO3)2·6H2O and no EDA.

The preparation of impregnated Co-S-1-zeolite(Imp-Co-S-1): Co atom supported on S-1 zeolite were prepared by impregnation method. Firstly, the calculated Co(NO3)2·6H2O was dissolved into 20 mL of deionized water. Then, same synthesized S-1 zeolite was put into the above solution and stirred for at 80 ℃ for 1hr. The mixture was evaporated under stirring for 1hr more and subsequently dried at 110 ℃ overnight. Finally, the dried sample was calcined in a muffle furnace at 550 ℃ for 4 h with a heating rate of 2 ℃ min^{-1}Oxygen carrier preparation.

Copper nitrate (Cu(NO3)2·6H2O, 99%), were obtained from Guoyao Chemical Reagent Co. Gamma Alumina carrier were obtained from Shanxi Juhua Co.

The preparation of copper modified oxygen carrier, using commercial alumina carrier, the carrier is first impregnated with 1M KOH with equal volume to obtain 2wt% K in solid, and then after calcination at 950℃ for 4hr, this is called base treatment, and then impregnated with saturated copper nitrate solution dried at 120℃ overnight, after calcined 750 degrees for 4 hours, the copper-containing oxygen carrier is prepared.

The obtained catalyst is in powder or granular form, and the particles used for characterization need to be further ground. As the catalyst and oxygen carrier, the powder sheet needs to be broken into 20-40 mesh for reaction evaluation.

2.2   Catalyst Characterization

The microstructure of the material was observed by JSM-7900F (JEOL) scanning electron microscope.

Nitrogen adsorption and desorption tests at low temperature were performed on a Micromeritics ASAP3020 fully automated physical adsorption instrument. Go up. Prior to analysis, the material was vacuumed at 300 °C for 6 hr. The specific surface area of the sample was calculated by Brunauer-Emmett-Teller (BET) method. The total pore capacity was calculated by the nitrogen adsorption at P/P0 = 0.98. The pore size distribution of the sample was calculated by BJH method using adsorption branch data.

The sample pyrolysis process and functional group decomposition components were analyzed by thermogravimetric mass spectrometry (TG-MS, Netzsch STA449 F5).

The crystal structure of the sample was scanned by XRD using CuKa at an Angle of 5-75° (2θ) and a scanning speed of 15 °/min. Panalytical X'Pert Pro X-ray diffractometer.

2.3   Catalyst Reaction Test

The evaluation of catalyst activity was carried out in a fixed-bed microreactor that could be heated up to max 650°C. The inner diameter of the quartz glass tube was 6mm, the catalyst loading dose was 0.4g, and mix with 0.8g quartz sand (for chemical looping oxidative dehydrogenation, it was replaced with oxygen carrier of the same weight), and quartz cotton was loaded both above and below. A thermal couple is loaded within the catalyst bed to ensure the bed temperature matches with oven temperature; a calibrated mass flowmeter is used to control C3H8 feed rate. Reaction conditions: feed is 100% pure propane, gas flow is 10ml/min, atmospheric pressure, reaction temperature is 580°C.

Typical operating steps are as follows: for the catalyst diluted with quartz sand, it is first heated to the reaction temperature in a nitrogen atmosphere within 1hr, and for the reaction that starts with the oxidation state, an air atmosphere is used during the heating process, flow rate is 50ml/min for both N2 and Air. After the reaction temperature is reached, purge N2 at 50ml/min for 10min for oxidative dehydrogenation experiments, for direct dehydrogenation experiments, this step is not necessary. Switch to 10ml/min C3H8 feed and maintain the reaction temperature, and after 7min of feeding, start to analyze the product. The product gas of the dehydrogenation process passes through the dehydrating device, only the generated water vapor is selectively removed, and then the remaining gas is analyzed by gas chromatography, in which the FID detector is used to analyze the hydrocarbon composition.

The catalyst activity is calculated as follows.

Propane Conversion X:

$$X(C3H8) = \frac{n_{C3H8}^{in} - n_{C3H8}^{out}}{n_{C3H8}^{in}} \tag{1}$$

Propylene Selectivity S:

$$S(C3H6) = \frac{n_{C3H6}^{in}}{n_{C3H8}^{in} - n_{C3H8}^{out}} \qquad (2)$$

3   Results and Discussion

3.1   Structural Properties

Both IS-Co-S-1 and Imp-Co-S-1 show good crystallinity, and the MFI features with 2θ between 23-25° have obvious characteristic peaks of MFI structure, see Figure 1. From the perspective of relative crystallinity, the relative crystallinity of in-situ synthesis is higher. the MFI structure crystallinity of the Imp-Co-S-1 is low, which may be due to the infect of the skeleton structure during the impregnation process.

No characteristic peak of Co-related structure was seen in the spectrum, which was mainly due to the low content of Co, and the highly dispersed Co element, which formed a strong structure with Si-O in S-1, so there was no Co-related peak in XRD spectrum.
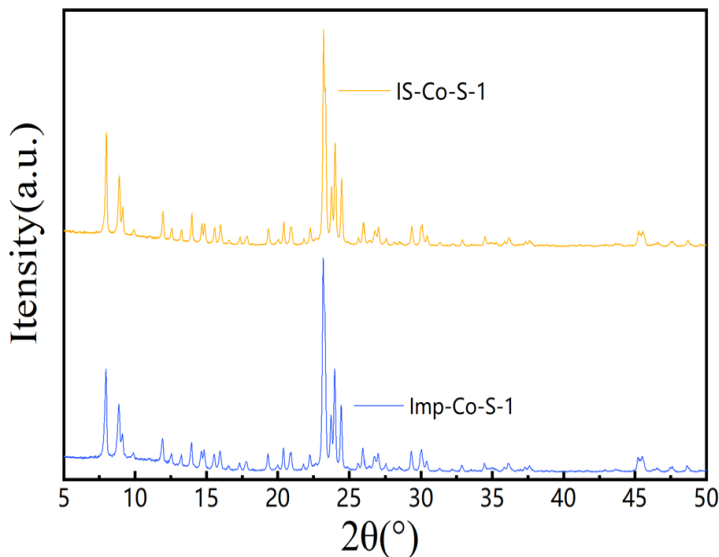
Fig. 1. XRD figure of Co-S-1 samples.

3.2   Pore Structure

From the adsorption and desorption curve, see Figure 2, that because Co replaces some Si atoms in the S-1 structure, a certain defect site is formed, so the formed zeolite has a certain mesoporous structure, which can be seen from the hysteresis loop of the nitrogen adsorption and desorption curve. Both Co-S-1 sample showed BET surface area between 400-420m2/g and pore volume of 0.32-0.35ml/g.

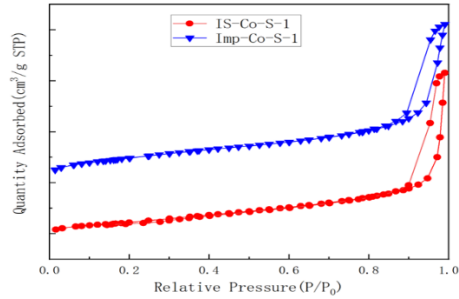The pore structure results are showed in Table 1:

Fig. 2. Nitrogen adsorption curve of Co-S-1.

Table 1. Pore structure of Co-S-1.

Sample	BET surface area (m²/g)	Pore Volume (ml/g)	XRF Co content (wt%)
IS-Co-S-1	412	0.331	1.07
Imp-Co-S-1	407	0.352	1.11

3.3   Morphology

As can see from the electron microscope images in Figure 3, the morphology of Co-S-1 synthesized in situ is more regular, and its crystal is more uniform, the particle size is about 500nm.

The surface morphology and appearance smoothness of Co-S-1 after impregnation in Figure 4 had some minor changes, and the particle size was basically the same as that of untreated ones, indicating that the impregnation and subsequent roasting of Co did not damage the skeleton structure of S-1, and the structure was intact.

Figure 5 showed the SEM picture of Cu supported Oxygen Carrier, the structure is similar with alumina base, and indicate that good dispersion of Cu.
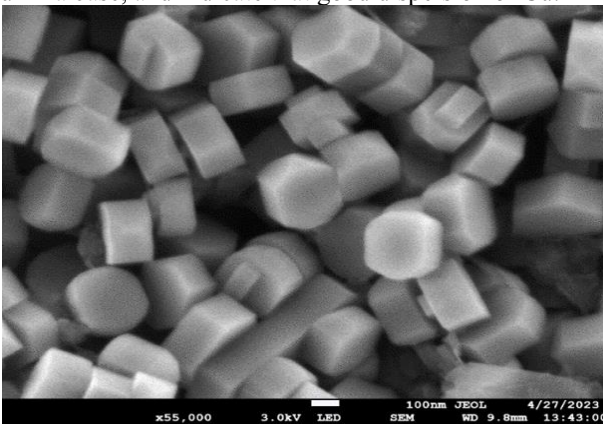
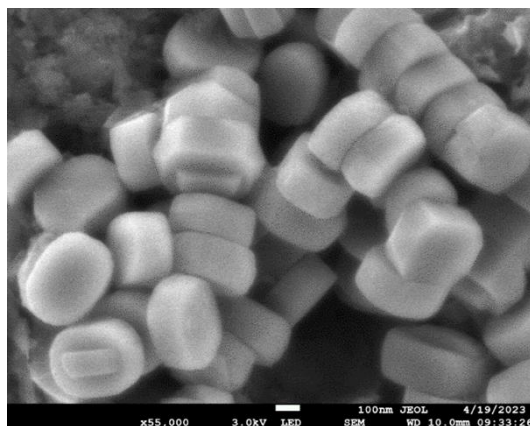**Fig. 3.** SEM figure of IS-Co-S-1.
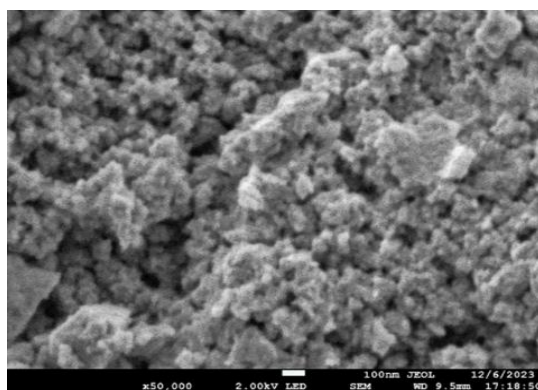
Fig. 4. SEM figure of Imp-Co-S-1.

Fig. 5. SEM figure of Cu supported Alumina base.

3.4   Catalytic Performance Result

Figure 6 shows catalyst performance result, at 580 degrees, two Co-S-1 samples both showed high reactivity, for IS-Co-S-1, the initial conversion is 25.3%, and gradually increase to 32.2%after 135min, and for Imp-Co-S-1, its initial conversion is 28.5% and increase to 32.4% after 102min, during this time the average selectivity is 94.1% for IS-Co-S-1 and 91.5% for Imp-Co-S-1. At the same time, the activity of the catalyst decreases a little with the deepening of the reaction time, which is mainly due to the carbon deposition on the catalyst surface.

   After coupled with the oxygen carrier, and the mass ratio is 1:2, for IS-Co-S-1, see figure 7, the conversion rate of the catalyst in the early stage of the reaction increased to a certain extent, the initial conversion increase from 25.2% to 32.2% by 7% and average conversion increase from 32.2% to 36.1% by 3.9%, mainly because the oxygen carrier consumed the hydrogen generated by the reaction, pulling and the chemical reaction carried out in the forward direction. After 100min, the reaction conversion

slightly decreased to a 34.2%. The selectivity remained unchanged at the corresponding time, average 94.1% comparing with 96.0% for IS-Co-S-1. This mainly attributed to t the water generated in the initial reaction inhibited the coking of the catalyst surface, thus improving the activity stability of the catalyst.

For Imp-Co-S-1, the result in figure 8 showed a similar trend as IS-Co-S-1, the difference is that the increment after mixing with oxygen carrier is higher, the initial conversion increase from 28.5% to 36.5% by 8% and average conversion increase from 32.4% to 36.5% by 4.5%. while the selectivity increases from 91.5% to 93.1%.

Comparing with IS-Co-S-1, Imp-Co-S-1 showed about 3% lower in selectivity, but its conversion increases 4.5% after coupled with oxygen carrier comparing 3.9% for IS-Co-S-1. this difference may due to Co atom in Imp-Co-S-1 is closer to outer surface as impregnation operations tend to form Co concentrated on outer surface.
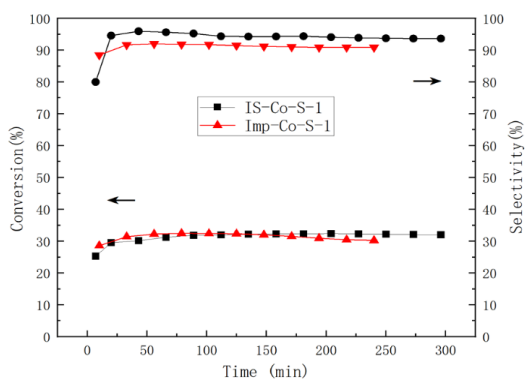

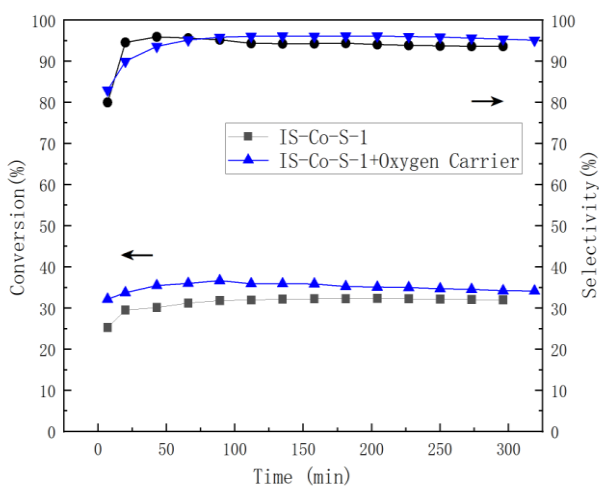**Fig. 6.** Direct Propane dehydrogenation reaction result for Co-S-1.

Fig. 7. Direct and Oxidative Propane dehydrogenation reaction result for IS-Co-S-1.
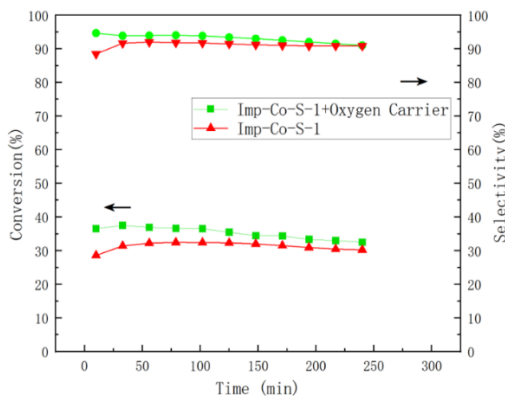
Fig. 8. Direct and Oxidative Propane dehydrogenation reaction result for Imp-Co-S-1.

4   Conclusion

In this study, supported copper oxygen carriers with high oxygen content were prepared by impregnation method and simple mixing method. 2 different types of Co-S-1 catalysts were prepared by in-situ synthesis method and impregnation modification method, and their properties were fully characterized. The prepared catalyst was tested and evaluated for single propane dehydrogenation and oxidative coupling dehydrogenation combined with oxygen carrier, and the following conclusions can be drawn:

First, the existence of oxygen carrier has a certain influence on oxidative dehydrogenation reaction. Oxygen carrier with inert material composite is more suitable for dehydrogenation reaction and can provide higher oxygen carrier.

Second, Co-S-1 not only exhibits high direct dehydrogenation activity, but also exhibits high oxidative coupling catalytic activity, which is mainly due to the binding of Co atoms and Si-O structure. In situ synthesis of CO-S-1 shows better reactivity, which is mainly due to better dispersity of Co formation.

Third, as the synthesis process of Imp-Co-S-1 also avoided complex in situ Co-S-1 hydrothermal synthesis process and may use commercial S-1 zeolite, and the impregnated Co-S-1 also has better reactivity, it showed potential of being used for industrial chemical looping oxidative dehydrogenation.

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