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Phosphorous-modified ordered mesoporous carbon for catalytic dehydrogenation of propane to propylene†

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Phosphorous (P)-modified ordered mesoporous carbon CMK-3 was used as a catalyst for the direct dehydrogenation (DH) of propane to propylene without any auxiliary stream, and this catalyst exhibited better activity and selectivity than the pristine ordered mesoporous carbon. The prepared samples were characterized by N₂ adsorption and desorption, temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). After the introduction of P using an impregnation method, P=O groups formed on the surface of the materials and substantially improved the activity and selectivity. The P=O groups are believed to be electron donors for C=O active centers, or independent active centers for catalytic DH of propane.

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Introduction

Propylene is a rather important intermediate for the production of polymers and other chemical compounds in petrochemical and polymer processes,^{1–3} and propylene is primarily produced by traditional steam cracking reactions or fluidized catalytic cracking (FCC). Dehydrogenation of propane is used in commercial operation using alumina-supported chromium or platinum catalysts promoted with an alkali.⁴ Other metal oxide catalysts (*e.g.*, V₂O₅ and MoO₃)^{5,6} and metal oxide supported zeolite catalysts (*e.g.*, Cr-MCM-41, V-SBA-15 and Zn-ZSM-5)^{7–9} have also been used for the dehydrogenation of propane. These processes are energy consuming with low selectivity that waste resources and product greenhouse gases. However, metal-free heterogeneous catalysis using carbon is considered to be an interesting alternative to some current industrialized chemical processes. Comparison to traditional metal catalysts, carbon catalysts are environmentally acceptable with inexhaustible resources.

Some carbon materials, such as carbon nanotubes, carbon fiber and mesoporous carbon, have recently attracted much interest for catalytic applications, and these materials were determined to be efficient in dehydrogenation reactions of ethylbenzene and alkanes due to their high surface area,

uniform pore size, high electron conductivity and functionalizable surfaces^{10–12} In addition to the common properties of carbon materials, the unique structural feature of ordered mesoporous carbons (OCM) is more easily accessible to gaseous activation molecules than those of conventional carbons, resulting in more efficient activation processes with functionalized sites. In addition, OCM with its high surface area and a uniform pore size facilitates the access of reactants to the active sites and allows for good reactant flux. The periodically arranged uniform mesopore space, alternative pore shapes, and tunable pore sizes^{13,14} of OMC materials make it a promising candidate for many applications. Yuan and co-workers¹⁵ studied catalytic dehydrogenation of propane to propylene with OMC catalysts and determined that OMC catalysts exhibited high activity and selectivity as well as good stability compared to carbon nanotube and graphite carbon catalysts. These results were due to surface carbonyl groups and well-ordered porosity of OMC catalysts, which was beneficial for mass transport and avoiding hot spots during catalytic reactions.^{13,16,17}

D. S. Su¹⁸ stated that in general, the termination of carbon sheets always requires foreign atoms to saturate dangling bonds, and therefore, the intrinsic properties of carbon materials could be readily modified by the introduction of heteroatoms to functionalize graphene geometries at defects, edges or strained regions.¹⁹ Many previous studies used carbon materials as catalysts doped with heteroatoms, such as P, B and N, to alter the performance of electrode materials, Fischer–Tropsch synthesis catalysts, and oxidative dehydrogenation catalysts.^{20–22} In these cases, doped heteroatoms improved the properties of the carbon materials by changing the electrical conductivity or oxidation reduction behavior of different functional groups.

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In the dehydrogenation process, the unsaturated and nucleophilic ketonic carbonyl groups (C=O) on the surface of carbon materials were considered to be the active sites and acted as electron donors to activate the C–H of alkanes. However, highly electrophilic oxygen groups would lead to total oxidation products. In the oxidative dehydrogenation (ODH) of low alkanes, carbon material catalysts promoted with P exhibited higher propylene selectivity compared to the pristine carbon catalysts. P may exert an influence by blocking certain sites, resulting in suppression of excessive activation that would lead to deep oxidation of the alkene substrates.^{19,23,24} However, no experimental data have been reported for P promoted OMC catalysts in the catalytic direct dehydrogenation (DH) of propane to propylene under oxygen-free reaction conditions. We developed carbon material catalysts for the catalytic DH of low alkanes to alkenes. Herein, we report the results for the catalytic behavior of P-modified OMC catalysts for the catalytic dehydrogenation of propane to propylene.

Results and discussion

The studies of the catalytic dehydrogenation of propane for propylene production were conducted under oxygen-free reaction conditions with different catalysts. The exit gases contained propane, propylene, methane, ethane, ethane and helium. In a blank test in the absence of a catalyst, the propane conversion was less than 1.3% at 873 K. The change in the propane conversion and propylene selectivity at different temperature for CMK-3 were exhibited in Fig. 1. The increased temperature affected the propane conversion and propylene selectivity. The propane conversion substantially increased with the increase of temperature. However the propylene selectivity decreased from 89 to 73%. The product distribution analysis indicated that the decrease in the propylene selectivity was due to further cracking of propylene to CH₄, C₂H₄, and C₂H₆ at higher temperatures. Therefore, the optimum reaction temperature for propane dehydrogenation based on these constraints was determined to be 873 K.

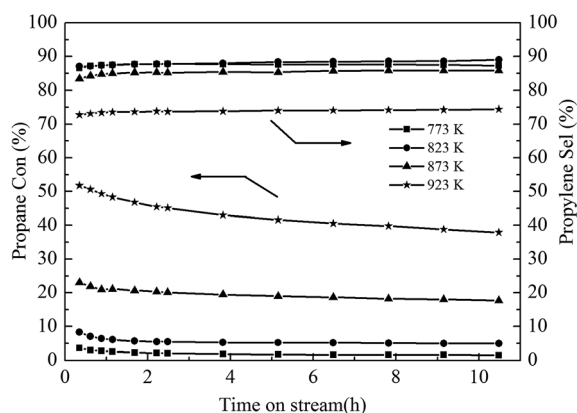


Fig. 1 Effect of temperature on the dehydrogenation of propane over CMK-3 (catalyst: 0.20 g, C₃H₈/He: 1/19 mL min⁻¹).

The variation in P doping had a significant influence on the mesoporous carbon for propane dehydrogenation to propylene (seeing Fig. 2). However propane conversion and propylene selectivity over 1%P/OCMK increased to a maximum and then decreased as the P loading increased. Comparison to a traditional noble metal catalyst (*i.e.*, Pt/OCMK), the activity of 1%P/OCMK was better than that of Pt/OCMK (Fig. S1†). At a high P loading level, (*i.e.*, 2%P/OCMK and 4%P/OCMK sample), the treatment caused a decrease in the BET surface areas and pore volumes, resulting in blockage of pores (Table 1s†).²³ Therefore the optimum P loading for propane DH was 1%. The N heteroatom was also used to modify CMK-3, the conversion of N/OCMK was much lower than that of 1%P/OCMK (Fig. S2†).

The changes in the propane conversion and propylene selectivity with time-on-stream (TOS) for all three tests are shown in Fig. 3. Because the operating conditions in the three tests were nearly the same, the obtained values for the propane conversion were indicative of the intrinsic catalyst activities in the three tests. The initial activity of P/OCMK catalyst at 873 K was 28% with 88% propylene selectivity, which is much higher than that of the CMK-3 and OCMK catalysts without P (15 and 17% propane conversion with 86 and 85% propylene selectivity, respectively). The activities of the pristine CMK-3 and OCMK catalysts were similar to each other within experimental error, which indicated that functionalized treatment with concentrated HNO₃ only had a limited effect on the activity of the CMK-3 materials. However after modification with P, the initial activity of the OCMK catalyst improved substantially from approximately 17 to 27%. However, at the very beginning, the rate of deactivation for all three catalysts was very high. During the overall tests that lasted 24 h, the activity of the 1%P/OCMK catalyst remained 5% higher than those of the CMK-3 and OCMK catalysts. These results are due to the promotion effect of P.

Fig. 4 shows the nitrogen adsorption–desorption isotherm curves and BJH pore size distributions of the three catalysts before and after the reaction. The nitrogen isotherms of the fresh and used OMC catalysts exhibited classical type IV isotherms with a well-defined hysteresis loop, which is characteristic of

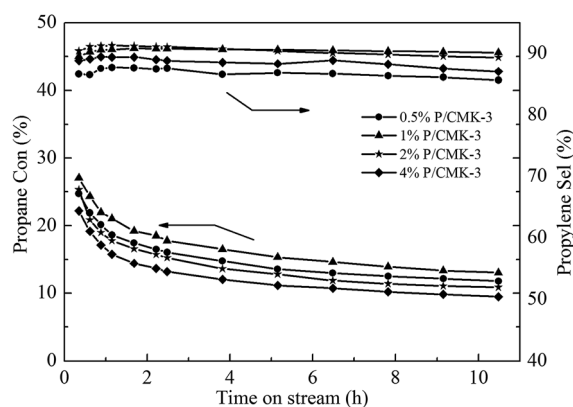


Fig. 2 Effect of P doping on the dehydrogenation of propane over P/OCMK (catalyst: 0.10 g, C₃H₈/He: 1/19 mL min⁻¹, reaction temperature: 873 K).

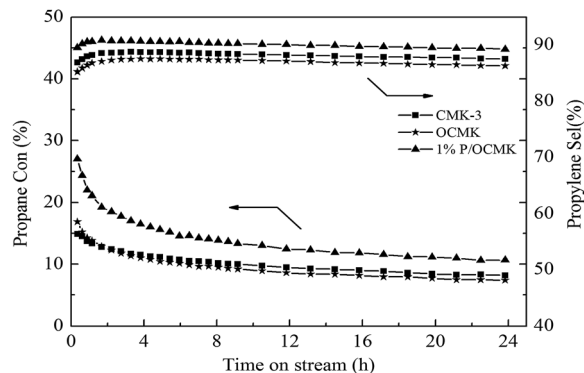


Fig. 3 Conversion and selectivity of dehydrogenation of propane to propylene over CMK-3, OCMK and 1%P/OCMK (catalyst: 0.10 g, C_3H_8/He : 1/19 mL min^{-1} , reaction temperature: 873 K).

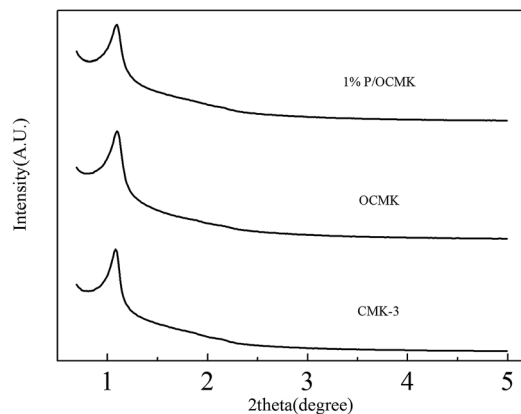


Fig. 5 Small XRD patterns of mesoporous carbon sample CMK-3, OCMK and 1%P/OCMK.

mesoporous materials. In addition, the large quantity adsorbed at the low $p/p_0 = 0-0.1$ indicated the presence of a large number of micropores. The ordered mesostructure was confirmed by the small-angle XRD patterns, which contained one peak (Fig. 5). The three samples exhibited a peak in the small-angle X-ray diffraction patterns, which confirmed the ordered mesostructure and indicated a similar mesopore size. According to the adsorption curves, the average distribution of the mesopore size for 1%P/OCMK was larger than that of other samples.

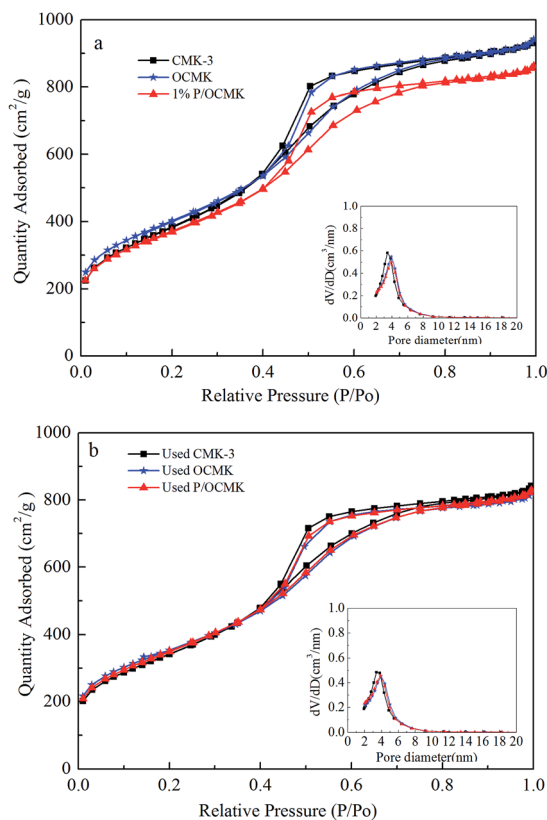


Fig. 4 Nitrogen adsorption-desorption isotherms of fresh (a) and used (b) catalysts.

The BET surface areas and pore volumes for all three samples are listed in Table 1. The BET surface area of the pristine CMK-3 material, the surface area most likely was decreased after addition of P possibly, which was due to the pore-filling and pore-blocking of channels during the impregnation treatment of with P.²³ After 24 h of operation, both the surface area and pore volume of all catalysts decreased some for all catalysts, which is possibly most likely ascribed due to coke formation during the DH test. Although 1%P/OCMK had possessed a smaller BET surface area and pore volume than CMK-3 and OCMK, its activity was as high as 12% propane conversion with 90% propylene selectivity after 24 h of operation, and these results much better than that of the CMK-3 and OCMK catalyst. To the best of our knowledge, coke formation can have a strong effect on the catalytic performance of carbon material catalysts and most likely led to catalyst deactivation.¹¹ Interestingly, after the test period that lasted 24 h, the mesopore surface area of the 1%P/OCMK catalyst remained the same. However, its micropore surface area decreased substantially, which indicated that the majority of the coke formed first in the micropore and had a limited effect on mesopore. The large and well-ordered mesoporous porosity of the ordered mesoporous carbon catalysts is beneficial for mass transport and avoiding hot spots during catalytic reactions of ordered mesoporous carbon catalysts. This result demonstrates the unique characteristic of the 1%P/OCMK catalyst during DH reaction.

To gain a better understanding of the surface chemistry after P modification, the surface compositions of the fresh and used catalyst were investigated using X-ray photoelectron

Table 1 Textural properties of CMK-3, OCMK and 1%P/OCMK

Sample	S_{BET} ($m^2 g^{-1}$)	S_{micro}	S_{meso}	V_{total} ($cm^3 g^{-1}$)
CMK-3	1384 ^b /1252 ^a	116 ^b /62 ^a	1268 ^b /1190 ^a	1.42 ^b /1.27 ^a
OCMK	1443 ^b /1271 ^a	126 ^b /107 ^a	1317 ^b /1164 ^a	1.42 ^b /1.24 ^a
1%P/OCMK	1338 ^b /1268 ^a	90 ^b /20 ^a	1248 ^b /1248 ^a	1.31 ^b /1.25 ^a

^a Values measured after the reaction. ^b Values measured before the reaction.

spectroscopy (XPS). As shown in Fig. 6a and c, the oxygen spectra were fitted to three peaks as follows:^{25,26} peak A (~ 531 eV) for double bonded oxygen ($=O$) in $C=O$ and $P=O$,²⁷ the peak B (~ 533 eV) for singly bonded oxygen ($-O-$) in $C-O$ and $C-O-P$,²² and the peak C (~ 535 eV) for chemisorbed oxygen and water.³ The area of peak A for 1%P/OCMK was twice that of CMK-3. The ratio of the area of peak A to the area of peak B increased after addition of phosphorous to CMK-3 (Fig. 6a and c), which demonstrated the formation of $P=O$ groups due to P modification. Fig. 7 shows the P2p spectra for 1%P/OCMK. Peaks B ($2P_{3/2}$) and C ($2P_{1/2}$) were used to fit the spectrum with a branching ratio of 2 : 1. The BE position of the $2P_{3/2}$ peak located at approximately 133 eV was due to pentavalent tetra-coordinated phosphorus (PO_4 tetrahedra).²⁸ The structure with $C-O-P$ bonding was much more stable and persisted longer than the structure with $C-P-O$ bonding at the high temperature and phosphates attached to carbon matrix by $C-O-P$ linkage,²⁸⁻³⁰ as shown in the P2p and O1s spectra. In comparison to the spectra of fresh catalyst, an additional peak (A) (Fig. 7b) was observed for the used catalyst due to P.²⁹ The P appearance indicated that the phosphate groups were reduced to P during the test. Although the reduction of phosphate groups occurred at higher temperatures of approximately around 1073 K,¹² the reductive atmosphere containing C_3H_8 , C_3H_6 and H_2 improved the reduction behavior of the phosphate groups, leading to the reduction of P at a slightly lower temperature.

The catalytic activity of the carbon material was related to its abundant surface oxygen groups, such as carboxyl, anhydride, hydroxyl, ketonic carbonyl and lactone groups.³¹⁻³³ Among these groups, the unsaturated and nucleophilic ketonic carbonyl groups ($C=O$) are regarded as the active sites, which can activate alkanes due to their electron property. In the dehydrogenation process, the ketonotic $C=O$ groups activated the $C-H$ bonds of propane to produce propylene and hydroxyl groups ($C-OH$), where the hydroxyl groups acted as reaction intermediates. The reaction cycle was closed by the decomposition of $C-OH$ to $C=O$ at the reaction temperature.³⁴ However, the electrophilic groups activated the unsaturated alkene (*i.e.*, C_3H_6) leading to

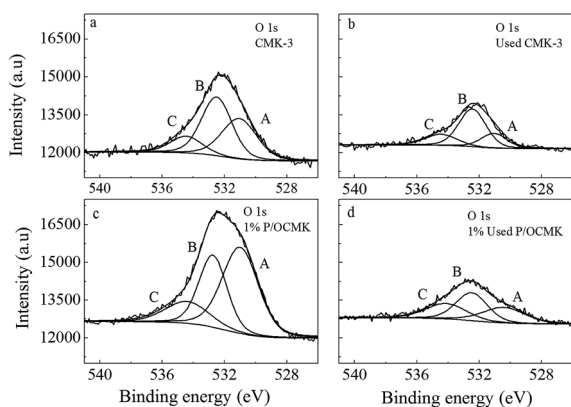


Fig. 6 XPS spectrum of O1s peak of fresh (a and c) and used catalysts (b and d).

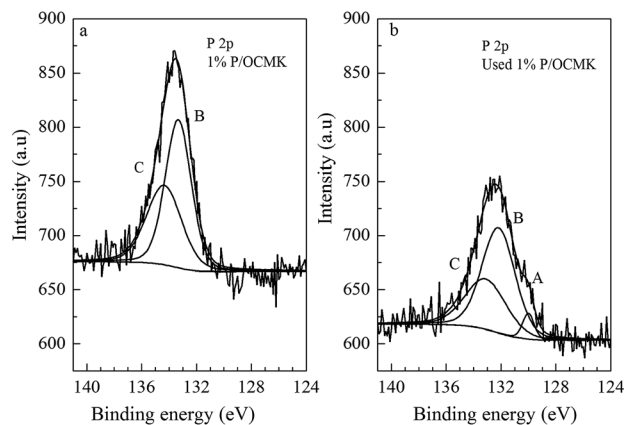


Fig. 7 XPS spectrum of P2P peak of fresh (a) and used catalysts (b).

deep cracking. The evolution of group species containing oxygen functions can be measured by TPD, and the results are shown in Fig. 8. In general, CO desorption resulted from the decomposition of phenol, ether, anhydride and ketonic carbonyl groups, however, CO_2 desorption was associated with carboxylic, lactone and anhydride groups.³⁵ Ketonic carbonyl groups were typically associated with CO desorption temperatures between 973 and 1253 K. Phenols, anhydrides and ethers decomposed at temperature lower than 927 K. Therefore, peak A (Fig. 8a) corresponding to CO desorption at approximately 927 K most likely originated from the decomposition of ethers, and peak B (Fig. 8a) corresponding to CO desorption at approximately 1073 K was due to the decomposition of ketonic carbonyl groups,³⁶ which indicated the existence of nucleophilic ketonic carbonyl groups in all three catalysts. In addition, as shown from XPS results, the phosphorus modification resulted in the formation of $C-O-PO_3$ groups on the 1%P/OCMK surface. The highly stable $C-O-PO_3$ groups can decompose to CO and phosphate at approximately 1073 K.^{23,29} Therefore, the stronger B peak of the 1%P/OCMK catalyst may be due to the simultaneous decomposition of ketonic carbonyl and $C-O-PO_3$ groups.

Fig. 8b shows CO_2 desorption spectra. The functional groups, such as carboxylic, anhydride and lactone, are desorbed at typical temperatures of 573, 773, and 973 K respectively. For 1%P/OCMK, an obvious shoulder peak (B), which was due to the decomposition of phosphate to CO_2 and P, was observed at 1070 K. This XPS spectrum also confirmed the existence of P. In addition, this temperature was consistent with the CO desorption spectra in Fig. 8a. The decomposition of the phosphate groups during the reaction led to a decrease in the amount of $P=O$ groups on the surface of mesoporous carbon, which may have contributed to the deactivation of 1%P/OCMK.

The amount of P before and after the reaction was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The P amount of 1%P/OCMK before and after reaction were 1.18% and 0.59%, respectively. After introduction of P using the impregnation method, $P=O$ groups formed on the surface of the materials and substantially improved the activity and selectivity. However, after the DH of propane, the inactivated 1%P/OCMK sample exhibits XPS peaks originating from

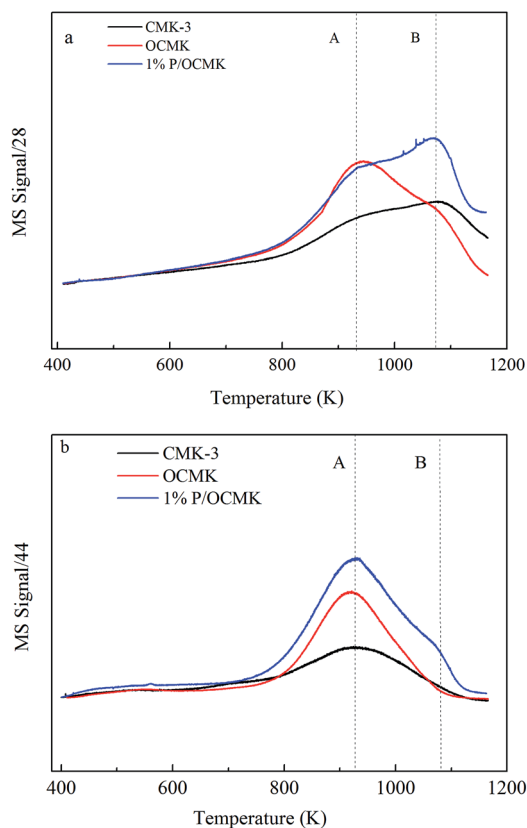


Fig. 8 TPD profile of catalyst showing traces of m/z at 28 (a) and 44 (b).

pentavalent tetra-coordinated phosphorus with a lower intensity and an additional peak corresponding to the P element. The P appearance indicated that the phosphate groups were reduced to P during the test. The element should evaporate resulting in a decrease in the P amount after the DH of propane. Combination with the reaction rate data, P modification can enhance the catalytic performance by introducing P=O groups. The P=O groups were believed are most likely electron donors for the C=O active centers, or independent active centers for catalytic DH of propane.

In previous studies of the oxidative DH reaction of alkanes to alkenes with P-modified carbon materials, the phosphorous groups did not typically alter the properties of the active sites on the surface of the carbon materials but affected the availability of the sites by blocking the catalytic combustion pathway and inhibiting the formation of CO_x products, which resulted in an increase in the alkene selectivity.^{18,19} However, in the current studies, the studies of the catalytic DH of propane to propylene with the P promoted catalyst were conducted under oxygen-free reaction condition. The P-modified CMK-3 catalyst still exhibited a higher activity and propylene selectivity compared to the other two ordered mesoporous catalysts without the P promoter. Due to the lack of molecular oxygen in the reactants, the deep oxidation reaction did not occur *via* the adsorption of molecular oxygen on defect or edge sites, resulting in the production of CO_x.²³ In addition, peak B

in Fig. 6a for 1%P/OCMK was much more intense than that of the other two catalysts, indicating the existence of large number of functional groups on the surface of the 1%P/OCMK. Because the preparation of the 1%P/OCMK catalyst was performed under a nitrogen atmosphere, the number of C=O groups cannot be increased during this process. Therefore, the increased amount of functional groups after P modification correspond to P=O groups. Both the C=O and P=O groups were vital for the DH reaction of propane, and the superior activity of 1%P/OCMK was due to the synergetic impact of these two groups. The effect of the heteroatoms on the properties of the OCMK catalysts may result from the modification of the electron affinity of the carbonyl/quinone groups over carbon surface, which are considered to be essential catalytic active sites. The P=O groups were electron donors and provided electrons to unsaturated C=O carbonyl groups. These groups received the electron and had a greater electron density on the oxygen atom and acted as a Lewis base to activate the paraffin,^{10,11,14,16} resulting in a higher activity compared to the other two catalysts.

In addition to the C=O groups, the P=O functional groups are another type of independent active center similar to C=O for the dehydrogenation reaction and catalytic activation of these C-H bond of propane. Therefore, the number of active sites on the surface of x P/OCMK for the DH reaction increased substantially. The x P/OCMK catalyst had many more active centers than CMK-3 and OCMK during the catalytic DH of propane, which was in good agreement with the experimental results shown in Fig. 3. The P groups over the x P/OCMK catalysts produced a positive effect on the catalytic DH of propane to propylene by providing electron to the C=O group as electron donor, and/or active centers for the direct activation of C-H bond of propane. Further studies using the CMK-3 catalysts promoted with P are in progress to determine the function of the P=O groups in the catalytic DH of propane to propylene.

Conclusion

In summary, P-modified ordered mesoporous carbon was successfully prepared and used in the catalytic dehydrogenation of propane to propylene. The catalyst modified by P which is referred to as x P/OCMK exhibited superior catalytic performance due to the formation of phosphate groups on the surface of the OCMK materials. Both the ketonic carbonyl (C=O) and phosphate (P=O) groups may be the key species during the propane activation process. The P=O groups acted as electron donating groups to the C=O groups, resulting in the activation of propane being more facile. In addition, the P=O functional groups were another type of independent active center for catalytic dehydrogenation reaction.

Experimental

Catalyst synthesis procedure

According to the report by R. Ryoo,³⁷ the ordered mesoporous carbon CMK-3 was synthesized using the nanocasting strategy with SBA-15 material and sucrose as the hard template and

carbon source, respectively. CMK-3 was stirred in a HNO₃ solution (2 M) for 2 h at ambient temperature, and the obtained catalyst OCMK was calcined at 873 K for 2 h in N₂. The activated CMK-3 is referred to as OCMK. P modified OCMK was prepared using the impregnation method with an aqueous solution containing the desired amount of (NH₄)₂HPO₄ followed by drying at 393 K for 12 h and calcining at 873 K for 2 h in N₂. The samples were labeled xP/OCMK, where x indicates the P/carbon support weight ratio (x = 0.5%, 1%, 2% and 4%). The nitrogen-doped catalysts (N/OCMK) were prepared by heat treatment of OCMK under flowing NH₃ at 1123 K for 1 h. 0.5Pt/OCMK was prepared using the impregnation method with an aqueous solution of consisting H₁₂N₆O₆Pt.

Catalyst characterization

The BET surface area and pore volume were obtained by nitrogen physisorption at 77 K using an ASAP2020 instrument (Micromeritics Corporation, USA). The samples were degassed at 553 K for 3 h prior to the measurements. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface areas (S_{BET}) at a relative pressure interval of $0.05 < P/P_0 < 0.3$, and the total pore volume (V_{total}) was determined at $P/P_0 = 0.98$.

The XRD pattern was recorded using a Bruker D2 Phaser instrument. The diffraction patterns were collected with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of $0.013^\circ \text{ s}^{-1}$. In a typical TPD experiment, an approximately 100 mg sample was placed in a U-tube reactor and purged with He (40 mL min^{-1}) at 383 K for 0.5 h, and then the temperature was ramped at a rate of 10 K min^{-1} from 383 to 1173 K. The produced CO and CO₂ were monitored by a quadrupole mass spectrometer.

X-ray photoelectron spectroscopy (XPS) was employed using a VG ESCALAB MK2 X-ray photoelectron spectrometer equipped with Al K α radiation ($h\nu = 1486.6 \text{ eV}$). The X-ray anode was operated at 250 W, and the high voltage was maintained at 12.5 kV with a detection angle of 90° . The pass energy was fixed at 50 eV for the high resolution spectra and the base pressure in the analysis chamber was $2 \times 10^{-8} \text{ Pa}$. The survey and multi region spectra were recorded for the C1s, O1s, and P2p photoelectron peaks. Peak XPS 4.1 software was used to fit the high resolution spectra.

The P loading of 1%P/OCMK before and after the reaction was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES 7300DV, PerkinElmer).

Catalyst tests

The experiments were performed in a quartz fixed-bed reactor packed with approximately 100 mg of catalyst at 873 K under atmospheric pressure. The feed composition was 5% C₃H₈ and diluted by He (total flow rate = 20 mL min^{-1}). The reaction products were analyzed on-line with an Agilent 6890N gas chromatograph (GC). The propane conversion (X) and propylene selectivity (S), expressed on a mol% carbon atom basis, are defined by the following equations:

$$X = \frac{n_{\text{C}_3\text{H}_8,\text{in}} - n_{\text{C}_3\text{H}_8,\text{out}}}{n_{\text{C}_3\text{H}_8,\text{in}}} \times 100\%, \quad S = \frac{n_{\text{C}_3\text{H}_6,\text{out}}}{n_{\text{C}_3\text{H}_8,\text{in}} - n_{\text{C}_3\text{H}_8,\text{out}}} \times 100\%$$

Acknowledgements

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References

- M. M. Bettahar, G. Costentin, L. Savary and J. C. Lavalley, *Appl. Catal., A*, 1996, **145**, 1–48.
- R. Grabowski, *Catal. Rev.: Sci. Eng.*, 2006, **48**, 199–268.
- J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, in *Physical Electronics Division*, ed. C. J. Eden Prairie, Perkin-Elmer Corporation, Eden Prairie, MN, 2nd edn, 1992, pp. 216–232.
- P. R. Pujado and B. V. Vora, *Hydrocarbon Process.*, 1990, **69**, 65–70.
- I. V. Mishakov, A. A. Vedyagin, A. F. Bedilo, V. I. Zaikovskii and K. J. Klabunde, *Catal. Today*, 2009, **144**, 278–284.
- F. Ivars, B. Solsona, E. Rodríguez-Castellón and J. M. López Nieto, *J. Catal.*, 2009, **262**, 35–43.
- Y. Ren, F. Zhang, W. Hua, Y. Yue and Z. Gao, *Catal. Today*, 2009, **148**, 316–322.
- Y. Ohishi, T. Kawabata, T. Shishido, K. Takaki, Q. Zhang, Y. Wang and K. Takehira, *J. Mol. Catal. A: Chem.*, 2005, **230**, 49–58.
- Y.-M. Liu, Y. Cao, N. Yi, W.-L. Feng, W.-L. Dai, S.-R. Yan, H.-Y. He and K.-N. Fan, *J. Catal.*, 2004, **224**, 417–428.
- M. F. R. Pereira, J. L. Figueiredo, J. J. M. Órfão, P. Serp, P. Kalck and Y. Kihn, *Carbon*, 2004, **42**, 2807–2813.
- P. Michorczyk, P. Kuśtrowski, P. Niebrzydowska and A. Wach, *Appl. Catal., A*, 2012, **445–446**, 321–328.
- B. Frank, M. Morassutto, R. Schomäcker, R. Schlögl and D. S. Su, *ChemCatChem*, 2010, **2**, 644–648.
- T. Y. Ma, L. Liu and Z. Y. Yuan, *Chem. Soc. Rev.*, 2013, **42**, 3977–4003.
- Y. Shi, Y. Wan and D. Zhao, *Chem. Soc. Rev.*, 2011, **40**, 3854–3878.
- L. Liu, Q. F. Deng, B. Agula, X. Zhao, T. Z. Ren and Z. Y. Yuan, *Chem. Commun.*, 2011, **47**, 8334–8336.
- D. S. Su, J. J. Delgado, X. Liu, D. Wang, R. Schlogl, L. F. Wang, Z. Zhang, Z. C. Shan and F. S. Xiao, *Chem.–Eur. J.*, 2009, **4**, 1108–1113.
- J. J. Delgado, X.-W. Chen, B. Frank, D. S. Su and R. Schlögl, *Catal. Today*, 2012, **186**, 93–98.
- D. S. Su, J. Zhang, B. Frank, A. Thomas, X. Wang, J. Paraknowitsch and R. Schlögl, *ChemSusChem*, 2010, **3**, 169–180.
- J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlogl and D. S. Su, *Science*, 2008, **322**, 73–77.
- X. C. Zhao, Q. Zhang, B. S. Zhang, C. M. Chen, A. Q. Wang, T. Zhang and D. S. Su, *J. Mater. Chem.*, 2012, **22**, 4963–4969.

- 21 X. Wang, J. S. Lee, Q. Zhu, J. Liu, Y. Wang and S. Dai, *Chem. Mater.*, 2010, **22**, 2178–2180.
- 22 X. Liu, B. Frank, W. Zhang, T. P. Cotter, R. Schlögl and D. S. Su, *Angew. Chem., Int. Ed.*, 2011, **50**, 3318–3322.
- 23 V. Schwartz, H. Xie, H. M. Meyer, S. H. Overbury and C. Liang, *Carbon*, 2011, **49**, 659–668.
- 24 B. Frank, J. Zhang, R. Blume, R. Schlögl and D. S. Su, *Angew. Chem., Int. Ed.*, 2009, **48**, 6913–6917.
- 25 Z. Spitalsky, D. Tasis, K. Papagelis and C. Galiotis, *Prog. Polym. Sci.*, 2010, **35**, 357–401.
- 26 L. Liu, Q. F. Deng, B. Agula, X. Zhao, T. Z. Ren and Z. Y. Yuan, *Chem. Commun.*, 2011, **47**, 8334–8336.
- 27 A. G. Kannan, N. R. Choudhury and N. K. Dutta, *Polymer*, 2007, **48**, 7078–7086.
- 28 M. Pelavin, D. N. Hendrickson, J. M. Hollander and W. L. Jolly, *J. Phys. Chem.*, 1970, **74**, 1116–1121.
- 29 A. M. Puziy, O. I. Poddubnaya, R. P. Socha, J. Gurgul and M. Wisniewski, *Carbon*, 2008, **46**, 2113–2123.
- 30 Y. J. Lee and L. R. Radovic, *Carbon*, 2003, **41**, 1987–1997.
- 31 G. Mestl, N. I. Maksimova, N. Keller, V. V. Roddatis and R. Schlögl, *Angew. Chem., Int. Ed.*, 2001, **40**, 2066–2068.
- 32 J. Delgado, D. Su, G. Reibmann, N. Keller, A. Gajovic and R. Schlögl, *J. Catal.*, 2006, **244**, 126–129.
- 33 J. Zhang, D. S. Su, R. Blume, R. Schlögl, R. Wang, X. Yang and A. Gajovic, *Angew. Chem., Int. Ed.*, 2010, **49**, 8640–8644.
- 34 J. H. Zhou, Z. J. Sui, J. Zhu, P. Li, C. De, Y. C. Dai and W. K. Yuan, *Carbon*, 2007, **45**, 785–796.
- 35 J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas and J. J. M. Órfão, *Carbon*, 1999, **37**, 1379–1389.
- 36 G. S. Szymański, Z. Karpiński, S. Biniak and A. Świątkowski, *Carbon*, 2002, **40**, 2627–2639.
- 37 S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712–10713.