BNL-107630-2015-JA

Submitted to: Topics in Catalysis

Replacing Precious Metals with Carbide Catalysts for Hydrogenation Reactions

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Abstract: Molybdenum carbide (Mo_2C and Ni/Mo_2C) catalysts were compared with Pd/SiO_2 for the hydrogenation of several diene molecules, 1,3- butadiene, 1,3- and 1,4-cyclohexadiene (CHD). Compared to Pd/SiO_2, Mo_2C showed similar hydrogenation rate for 1,3-butadiene and 1,3-CHD and even higher rate for 1,4-CHD, but with significant deactivation rate for 1,3-CHD hydrogenation. However, the hydrogenation activity of Mo_2C could be completely regenerated by H_2 treatment at 723 K for the three molecules. The Ni modified Mo_2C catalysts retained similar activity for 1,3-butadiene hydrogenation with significantly enhanced selectivity for 1-butene production. The 1-butene selectivity increased with increasing Ni loading below 15%. Among the Ni modified Mo_2C catalysts, 8.6%Ni/Mo_2C showed the highest selectivity to 1-butene, which was even higher selectivity than that over Pd/SiO_2. Compared to Pd/SiO_2, both Mo_2C and Ni/Mo_2C showed combined advantages in hydrogenation activity and catalyst cost reduction, demonstrating the potential to use less expensive carbide catalysts to replace precious metals for hydrogenation reactions.

Keywords: Selective hydrogenation; 1,3-Buatdiene; Cyclohexadiene; Carbides

1. Introduction

In manufacturing polymers, the catalytic hydrogenation of dienes is widely used for the purification of olefin stream. The hydrogenation catalysts commonly utilize supported precious metals, such as Pd-[1-3], Pt-[4-6], Rh-[7] or Au-[8, 9] based catalysts. The precious metal catalysts have shown high activity; however, their high cost and limited abundance are potential concerns for industrial applications. By forming bimetallic structures with a non-precious metal, the precious metal based catalysts could be enhanced in activity, thus lowering the catalyst cost. For example, by alloying Ni with Pd[10] or Pt[11, 12], the activity in 1,3-butadiene hydrogenation could be increased. Recently, the $Al_{13}Fe_4$ surface[13] was found to be active in 1,3-butadiene hydrogenation under ultra-high vacuum environment, demonstrating the feasibility of using non-precious metal catalysts for diene hydrogenation.

Another class of non-precious metal hydrogenation catalysts are carbides of early transition metals, which often show catalytic properties similar to those of precious metals[14, 15]. For example, molybdenum carbide (Mo_2C) was found to be active in hydrogenation-related reactions, such as hydrodeoxygenation (HDO) [16-18], hydrodesulfurization (HDS) [18-20], and aromatic compound hydrogenations[18, 21-24]. However, to the best of our knowledge non-precious metal carbides have not been explored for the hydrogenation of dienes.

Moreover, according to previous studies [10, 11], the addition of Ni into the precious metal catalysts would enhance the catalytic performance in the hydrogenation of 1,3-butadiene. Therefore Ni modified Mo_2C was also studied in the current paper to further explore the enhancement by Ni addition.

In the current study, we explored the possibility of replacing precious metals by molybdenum carbide (Mo_2C) for the hydrogenation of 1,3-butadiene, 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD) in a batch reactor, using a supported Pd/SiO_2 catalyst as a reference for comparison. Selective hydrogenation of 1,3-butadiene is an important reaction in industry for the purification of butene stream[25], while 1,3 and 1,4-CHDs are important reaction

intermediates for hydrogen storage through hydrogenation-dehydrogenation of cyclic hydrocarbons[26]. The Mo_2C catalyst was further modified by Ni to determine the effect of metal modification on the hydrogenation activity and selectivity of 1,3-butadiene.

2. Experimental

2.1. Catalyst preparation

High surface area SiO_2 (Alfa Aesar, Stock#44741,160 m^2/g) supported Pd catalyst was synthesized by incipient wetness impregnation, using $Pd(NO_3)_2 \cdot 2H_2O$ (Alfa Aesar) as precursor. The metal loading was 0.91% by weight.

Unsupported Mo_2C was synthesized by a temperature programmed carburization procedure from MoO_3, which was obtained by calcining ammonium molybdate (para) tetrahydrate (Alfa Aesar) in a static muffle furnace at 623 K for 6 hours. The MoO_3 powder was placed in a tube furnace flowing with 20% CH_4/H_2. The total flow rate was 155 cm^3 min^{-1} for 1g MoO_3. The temperature was ramped from room temperature to 873 K at 2 K/min, and was held for 2 hours. The CH_4 stream was cut off after the first hour at 873 K, allowing only H_2 flow to remove the extra carbon deposits on the surface of Mo_2C. After cooling to room temperature, the gas flow was switched to 1% O_2 in N_2 to passivate the surface defect sites before exposing the catalysts to air.

The Ni modified Mo_2C catalysts were synthesized by impregnating Ni onto MoO_3 using $Ni(NO_3)_2 \cdot 6H_2O$ as precursor. The Ni/MoO_3 powder was then placed into the tube furnace. The temperature program and the gas flow were the same as those in the synthesis of Mo_2C.

2.2. Characterization

The Mo_2C catalyst was characterized using X-ray diffraction (XRD), N_2 physisorption by Brunauer–Emmett–Teller (BET) theory, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The surface area of the support was determined by BET using N_2 adsorption-desorption on an Autosorb-1-C instrument. TEM measurements were performed using a JEM-2010 (JEOL Ltd., Tokyo, Japan) operated at 120 kV. The catalyst samples were prepared for imaging by

grinding and suspending ~1 mg of the reduced catalyst in ~5 mL of ethanol. A pipette was then used to collect the sample from the top of this suspension. Two drops of this solution were deposited onto a lacey support film and dried for 0.5 hour before the TEM measurement. SEM measurements were performed using a JSM 7401F (JEOL Ltd., Tokyo, Japan) instrument operated at 3.0 kV.

2.3. Catalytic evaluation

The hydrogenation activity was evaluated in a batch reactor which was equipped with Fourier transform infrared (FT-IR) spectroscopy. FT-IR was used to monitor the gas-phase concentrations of reactants and products during the hydrogenation reaction. The FT-IR spectra were recorded with 4 cm^{-1} resolution using a Thermo Nicolet Nexus 470 spectrometer equipped with a mercury cadmium telluride (MCT-A) detector. For all FT-IR experiments, ~14 mg of powder catalyst was loaded into the IR cell, which was then evacuated for 12 hours, until the system reached a pressure below 10^{-4} Pa. The catalysts were reduced at 723 K in 4000 Pa hydrogen for 30 minutes and the cell was then evacuated, followed by a high temperature flash (723 K) to remove any surface species generated during the reduction period. The reduction cycle was repeated three times before performing the hydrogenation experiments. After reducing the catalyst, 1040 Pa diene, 2293 Pa H_2 and 3333 Pa He were introduced into the reaction vessel simultaneously, with a diene to hydrogen ratio of 1:2.2. The reaction proceeded in gas phase at a catalyst temperature of 308 K and a total pressure of 6666 Pa. The catalyst was held static during the reaction. Details of the reactor and the FT-IR detection of the gas-phase components were reported elsewhere[11]. In the regeneration experiments, the Mo_2C catalsyt was regenerated in 9333 Pa H_2 by performing the same procedure as in the reduction. The reactivity data were collected in the reaction controlled regime because the reactions were measured at a very low starting conversion and the transport should not play a role.

In the current study, the reactions are denoted as follows:

$$C_4H_6 + H_2 \rightarrow C_4H_8 \qquad \text{(Reaction 1)}$$

$$C_4H_8 + H_2 \rightarrow C_4H_{10} \qquad \text{(Reaction 2)}$$

A first order rate law was used to fit the experimental data and to compare trend between different catalysts. According to previous studies [10, 11], the first order reaction showed a good fit of the experimental data of 1,3-butadiene consumption, and the derived reaction rate constants were useful for comparing the trend in different catalysts. For example, the rate laws for the first step and second step hydrogenation of 1,3-butadiene are:

$$\frac{dC_A}{dt} = -r_1 = -mk_1C_A \qquad \text{(Eq 1)}$$

$$\frac{dC_B}{dt} = r_1 - r_2 = mk_1C_A - mk_2C_B \qquad \text{(Eq 2)}$$

where C_A is the concentration of 1,3-butadiene, C_B is the concentration of 1-butene, and m is the weight of catalyst. The concentration of 1,3-butadiene and 1-butene are obtained by integrating Eqs (1) and (2):

$$\frac{C_A}{C_{A0}} = e^{-mk_1t} \qquad \text{(Eq 3)}$$

$$\frac{C_B}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-mk_1t} - e^{-mk_2t}\right) \qquad \text{(Eq 4)}$$

3. Results and Discussion

3.1. Characterization

The characterization results of Mo_2C are shown in Fig. 1. The XRD patterns confirm the formation of β-Mo_2C (JCPDS: 35-0787) (1a). The 2θ values of 34.1, 37.6, 39.5, 52.0, 61.7, 69.5, 74.6, and 75.9 correspond to the (100), (002), (101), (102), (110), (103), (112), and (201) facets of β-Mo_2C, respectively. The TEM image shows the lattice of Mo_2C (1b), with the 0.23 nm and the 0.26 nm distances corresponding to the (101) and (100) facets, respectively. The Mo_2C catalyst as synthesized has a low surface area of 5.0 m^2/g by BET analysis (1c) and the relatively flat surfaces of the Mo_2C particles are shown in the SEM image (1d). The particle sizes of Mo_2C and Ni/Mo_2C are 0.5 – 1.5 μm.

3.2. Hydrogenation reactions over Mo_2C

During the diene hydrogenation reactions in a batch reactor, the gas-phase concentrations of reactants and products are monitored by FT-IR online. Fig. 2 shows the consumption rate of 1,3-butadiene, 1,3-CHD and 1,4-CHD as a function of reaction time. Compared to Pd/SiO_2, Mo_2C shows a similar consumption rate of 1,3-butadiene as Pd/SiO_2 (Fig. 2(a)), a similar initial consumption rate of 1,3-CHD (Fig. 2(b)) and a higher consumption rate of 1,4-CHD (Fig. 2(c)).

To make quantitative analysis of hydrogenation activity and rate of deactivation, the hydrogenation reaction rates are estimated by a first order rate law with a second order deactivation for the consumption of reactant dienes, and are normalized by catalyst weight. A second order deactivation model was used to fit the experimental data and to compare the deactivation between different catalysts. It has been found that the second order deactivation fits well for the hydrogenation reactions according to a previous study [27]. The kinetic models for determining the hydrogenation and deactivation rate constants are the same as those described for 1,3-butadiene in a previous study[27]. The normalized rate constants are summarized in Table 1. The reaction rate (k_r) over Mo_2C is 13% - 30% lower than that over Pd/SiO_2 for 1,3-butadiene and 1,3-CHD hydrogenation reactions, and is 2.9 times higher than that over Pd/SiO_2 for 1,4-CHD hydrogenation. The deactivation rate (k_d) over Mo_2C is generally higher than that over Pd/SiO_2 for the three diene molecules. For 1,3-butadiene and 1,4-CHD hydrogenation, the deactivation is almost absent over Pd/SiO_2, and is slightly higher over Mo_2C; however for 1,3-CHD hydrogenation, the deactivation is rather significant over both Pd/SiO_2 and Mo_2C.

The different performance in the hydrogenation reactions is most likely due to the molecular structures. 1,3-butadiene and 1,3-CHD contain conjugated structure and 1,3-CHD and 1,4-CHD contain cyclic structure. The reaction rate of conjugated dienes over Mo_2C is slightly lower than that over Pd/SiO_2, while the reaction rate of unconjugated diene over Mo_2C is higher than that over Pd/SiO_2. Compared with 1,3-CHD, the higher activity for 1,4-CHD over Mo_2C indicates that the conjugation in the diene molecules reduces the Mo_2C hydrogenation activity. On the other hand, the

deactivation rate for the three molecules follows the trend of 1,3-butadiene < 1,4-CHD < 1,3-CHD, implying that the deactivation rate in the hydrogenation of cyclic dienes is higher than that in the hydrogenation of linear diene, and that the conjugated diene is more easily to deactivate the catalysts than the corresponding unconjugated diene. Assuming that benzene is the precursor for coke formation, 1,3-CHD should have the molecular structure (both cyclic and conjugated) most facile to produce benzene and therefore leading to a faster catalyst deactivation. Other than the molecular structures, the different performance in the hydrogenation reactions might also be related to the different binding structures of the diene molecules on the different catalytic surfaces. The different surface areas of Pd/SiO_2 and the Mo_2C catalysts might also lead to differences in the hydrogenation activity and selectivity.

Although Mo_2C is more easily deactivated than Pd/SiO_2, it could be completely regenerated by H_2-treatment at 723 K. After performing H_2-treatment of the deactivated Mo_2C catalyst, the consumption curves for the three dienes were very similar to those with the fresh Mo_2C catalyst (profiles not shown), while the Pd-based catalysts could not be completely regenerated in alkyne/diene hydrogenation reactions due to a complex metal-carbonaceous interaction[9]. Therefore, Mo_2C is potentially a promising catalyst for diene hydrogenations in terms of both activity and catalytic regeneration.

3.3. Ni modification for the hydrogenation of 1,3-butadiene

The hydrogenation of 1,3-butadiene is used as a probe reaction to evaluate the effect of metal modification on the hydrogenation activity and selectivity of Mo_2C. In 1,3-butadiene hydrogenation, it is nessesary to optimize selectivity to 1-butene, which is the desired hydrogenation product. The 1-butene and butane concentration curves of Pd/SiO_2 and Mo_2C are plotted in Figs. 3(b)&(c). Although the hydrogenation rates of 1,3-butadiene are similar over Pd/SiO_2 and Mo_2C, the 1-butene concenration curves in Fig. 3(b) show a much lower 1-butene peak over Mo_2C, indicating a higher 1-butene hydrogenation rate and a lower 1-butene selectivity. It has been reported that Ni modification on Pd-based catalyst enhances the 1-butene selectivity[10]. Therefore

Ni was introduced to the Mo_2C catalyst for the improvement of the 1-butene selectivity.

Different loadings (1.5%, 6.7%, 8.6%, 15% w.t.) of Ni were impregnated onto Mo_2C. The Ni/Mo_2C catalysts were evaluated in the batch reactor and the rate constants of the first hydrogenation step (k_1: 1,3-butadiene → 1-butene) and the second hydrogenation step (k_2: 1-butene → butane) were estimated by a first order law according to Eqs (3) and (4). The values of k_1, k_2 and the selectivity (k_1/k_2) are compared in Fig. 4 as a function of Ni loading. The corresponding rate constants and the selectivities of Mo_2C and Pd/SiO_2 are also included as references (Ni loading is 0 for Mo_2C). As shown in Fig. 4, with increasing Ni loading, the 1,3-butadiene hydrogenation rate remains nearly the same but the 1-butene hydrogenation rate decreases significantly. As a result, the 1-butene selectivity increases with increasing Ni loading. When Ni loading increases to 6.7%, the selectivity reaches the same level of Pd/SiO_2. At a Ni loading of 8.6%, the selectivity is 0.43, which is higher than Pd/SiO_2. When Ni loading further increases to 15%, the 1,3-butadiene and 1-butene hydrogenation rates both decrease and the selectivity decreases slightly.

In general, the Ni/Mo_2C catalysts retain similar 1,3-butadiene hydrogenation activity as Mo_2C at Ni loadings lower than 15%. However on 15%Ni/Mo_2C, the 1,3-butadiene hydrogenation rate constant is only 2.7 $min^{-1} \cdot g\ cat^{-1}$, which is significantly lower than on Mo_2C (4.2 $min^{-1} \cdot g\ cat^{-1}$). The large loading of Ni likely covers some active sites on Mo_2C and inhibits the 1,3-butadiene hydrogenation. On the other hand, increasing Ni loading leads to a decrease in 1-butene hydrogenation activity, even at low Ni loadings. The different modification effects of Ni on the hydrogenation rate constants of 1,3-butadiene (k_1) and 1-butene (k_2) are responsible for the enhanced selectivity for 1-butene production.

Comparing the four investigated Ni/Mo_2C catalysts, the 1-butene selectivity of 8.6%Ni/Mo_2C is the highest and the 1,3-butadiene hydrogenation activity is still close to Pd/SiO_2. The selectivities of Mo_2C and 8.6%Ni/Mo_2C are compared with Pd/SiO_2 and Ni/SiO_2 in Table 2. The 1-butene selectivity is 0.22 over Ni/SiO_2 and is 0.11 over Mo_2C, which are both lower than the selectivity of 8.6%Ni/Mo_2C, indicating that the

higher selectivity over Ni/Mo_2C does not come from the separate effect of Mo_2C or Ni.

In a previous study the 1-butene selectivity was enhanced by modification of Ni in Ni-Pd/γ-Al_2O_3 bimetallic catalysts, and the higher 1-butene selectivity was attributed to the lower binding energy of 1-butene on the Ni-Pd bimetallic structure than on monometallic Pd [10]. Furthermore, Ma et al. [28] reported that Ni showed strong interaction with Mo_2C on Ni/Mo_2C, and Porosoff et al [29] reported that Co formed a $CoMoC_yO_z$ phase on Co/Mo_2C, which might also occur in the case of Ni/Mo_2C. Both studies suggest that the interaction of Ni with Mo_2C should modify the surface electronic properties, possibly leading to a decrease in 1-butene adsorption energy and thus increasing the selectivity.

3.4. Potential advantage in catalyst cost reduction

Since the Ni/Mo_2C catalyst shows advantage in the selective hydrogenation of 1,3-butadiene, it is important to make a general comparison with Pd/SiO_2 considering both catalyst cost and activity. Cost evaluation is made for Pd/SiO_2, Mo_2C and 8.6%Ni/Mo_2C and the results are summarized in Table 3. Here a factor α is defined as follows to compare the catalysts in combining both cost and activity:

$$\alpha = \frac{\text{Price of catalyt (USD·kg cat}^{-1}\text{)}}{\text{Normalized rate constant (min}^{-1}\text{·g cat}^{-1}\text{)}} \qquad \text{(Eq 5)}$$

As shown in Table 3, by replacing the precious metal with non-precious metal carbide, the value of α decreases by a factor of ~4, from 0.039 to 0.009 USD·min. However, the Mo_2C catalyst shows lower selectivity towards 1-butene than Pd/SiO_2, suggesting the limitation of replacing the precious metal catalysts by Mo_2C. By modifying Mo_2C with Ni, the selectivity increases to the same value of Pd/SiO_2. When the Ni loading is 8.6%, the selectivity is even higher than Pd/SiO_2. Meanwhile, the value α remains similar compared to Mo_2C. The higher 1-butene selectivity and the combined enhancement of activity and cost reduction of Ni/Mo_2C over Pd/SiO_2 suggest possible replacement of precious metal catalysts by Ni modified non-precious metal carbide catalysts.

4. Conclusions

In conclusion, the catalytic hydrogenation of 1,3-butadiene, 1,3-CHD and 1,4-CHD have been compared over Pd/SiO_2 and Mo_2C. The results show that Mo_2C has similar hydrogenation rate for 1,3-butadiene and 1,3-CHD, and even higher hydrogenation rate for 1,4-CHD. For 1,3-butadine hydrogenation, although Mo_2C shows similar activity with Pd/SiO_2, it gives lower selectivity to 1-butene. The Ni-modified Mo_2C catalysts significantly enhance the 1-butene selectivity, with 8.6%Ni/Mo_2C showing the highest selectivity.

Overall, both the Mo_2C and Ni/Mo_2C catalysts show enhancement in combination of activity and catalyst cost reduction. In particular, the combined advantages in activity, selectivity and cost reduction of Ni/Mo_2C demonstrate the potential to use less expensive catalysts to replace precious metals for selective hydrogenation reactions.

Acknowledgements

The work at Columbia University was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy, Office of Basic Energy Sciences. R. Hou was sponsored by China Scholarship Council. T.F. Wang was supported by Program for New Century Excellent Talents in University of China (NCET-12-0297).

References

[1] Furlong BK, Hightower JW, Chan TYL, Sarkany A, Guczi L (1994) Appl Catal A, 117: 41-51.

[2] Kripylo P, Turek F, Hempe KD, Kirmse H (1975) Chem Tech (Leipzig) 27: 675-679.

[3] Hightower JW, Furlong B, Sarkany A, Guczi L (1993) Stud Surf Sci Catal 75: 2305-2308.

[4] Sarkany A, Stefler G, Hightower JW (1995) Appl Catal A, 127: 77-92.

[5] Qi S, Yu W, Lonergan WW, Yang B, Chen JG (2010) Chin J Catal 31: 955-960.

[6] Qi S, Yu W, Lonergan WW, Yang B, Chen JG (2010) ChemCatChem, 2: 625-628.

[7] Schrock RR, Osborn JA (1976) J Am Chem Soc 98: 4450-4455.

[8] Miura H, Terasaka M, Oki K, Matsuda T (1993) Stud Surf Sci Catal 75: 2379-2382.

[9] Hugon A, Delannoy L, Krafft J-M, Louis C (2010) The Journal of Physical Chemistry C, 114: 10823-10835.

[10] Hou R, Yu W, Porosoff MD, Chen JG, Wang T (2014) J Catal 316: 1-10.

[11] Lonergan WW, Vlachos DG, Chen JG (2010) J Catal 271: 239-250.

[12] Lonergan WW, Xing XJ, Zheng RY, Qi ST, Huang B, Chen JG (2011) Catal Today 160: 61-69.

[13] Piccolo L (2013) Chem Commun 49: 9149-9151.

[14] Hwu HH, Chen JG (2005) Chem Rev 105: 185-212.

[15] Oyama S (1992) Catal Today 15: 179-200.

[16] Ren H, Yu W, Salciccioli M, Chen Y, Huang Y, Xiong K, Vlachos DG, Chen JG (2013) ChemSusChem, 6: 798-801.

[17] Boullosa-Eiras S, Lødeng R, Bergem H, Stöcker M, Hannevold L, Blekkan EA (2014) Catal Today 223: 44-53.

[18] Dhandapani B, St Clair T, Oyama S (1998) Appl Catal A, 168: 219-228.

[19] McCrea KR, Logan JW, Tarbuck TL, Heiser JL, Bussell ME (1997) J Catal 171: 255-267.

[20] Szymańska-Kolasa A, Lewandowski M, Sayag C, Djéga-Mariadassou G (2007) Catal Today 119: 7-12.

[21] Lee JS, Yeom MH, Park KY, Nam I-S, Chung JS, Kim YG, Moon SH (1991) J Catal 128: 126-136.

[22] Da Costa P, Potvin C, Manoli JM, Breysse M, Djéga-Mariadassou G (2001) Catal Lett 72: 91-97.

[23] St. Clair T, Dhandapani B, Oyama ST (1999) Catal Lett 58: 169-171.

[24] Mamède AS, Giraudon JM, Löfberg A, Leclercq L, Leclercq G (2002) Appl Catal A, 227: 73-82.

[25] Alves JA, Bressa SP, Martinez OM, Barreto GF (2004) Chem Eng J 99: 45-51.

[26] Schlapbach L, Züttel A (2001) Nature, 414: 353-358.

[27] Wang T, Mpourmpakis G, Lonergan WW, Vlachos DG, Chen JG (2013) Phys Chem Chem Phys 15: 12156-12164.

[28] Ma YF, Guan GQ, Phanthong P, Hao XG, Huang W, Tsutsumi A, Kusakabe K, Abudula A (2014) J Phys Chem C 118: 9485-9496.

[29] Porosoff MD, Yang X, Boscoboinik JA, Chen JG (2014) Angew Chem Int Ed 126: 6823-6827.

Figure Captions

Fig. 1 Characterizations of Mo_2C: (a) XRD; (b) TEM; (c) BET; (d) SEM

Fig. 2 Consumption rate of (a) 1,3-butadiene (b) 1,3-CHD (c) 1,4-CHD over Mo_2C. (T = 308 K, P_{H2} = 2293 Pa, P_{Diene} = 1040 Pa, and P_{He} = 3333 Pa)

Fig. 3 Consumption rate of (a) 1,3-butadiene and production rates of (b) 1-butene and (c) butane. (T = 308 K, P_{H2} = 2293 Pa, P_{Diene} = 1040 Pa, and P_{He} = 3333 Pa)

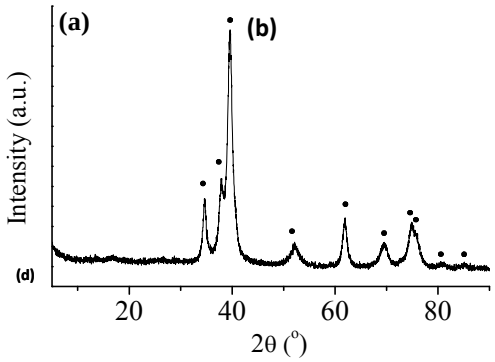
Fig. 4 Normalized reaction rate constants and the estimated selectivity on different loadings of Ni/Mo_2C (k_1: 1,3-butadiene → 1-butene; k_2: 1-butene → butane)

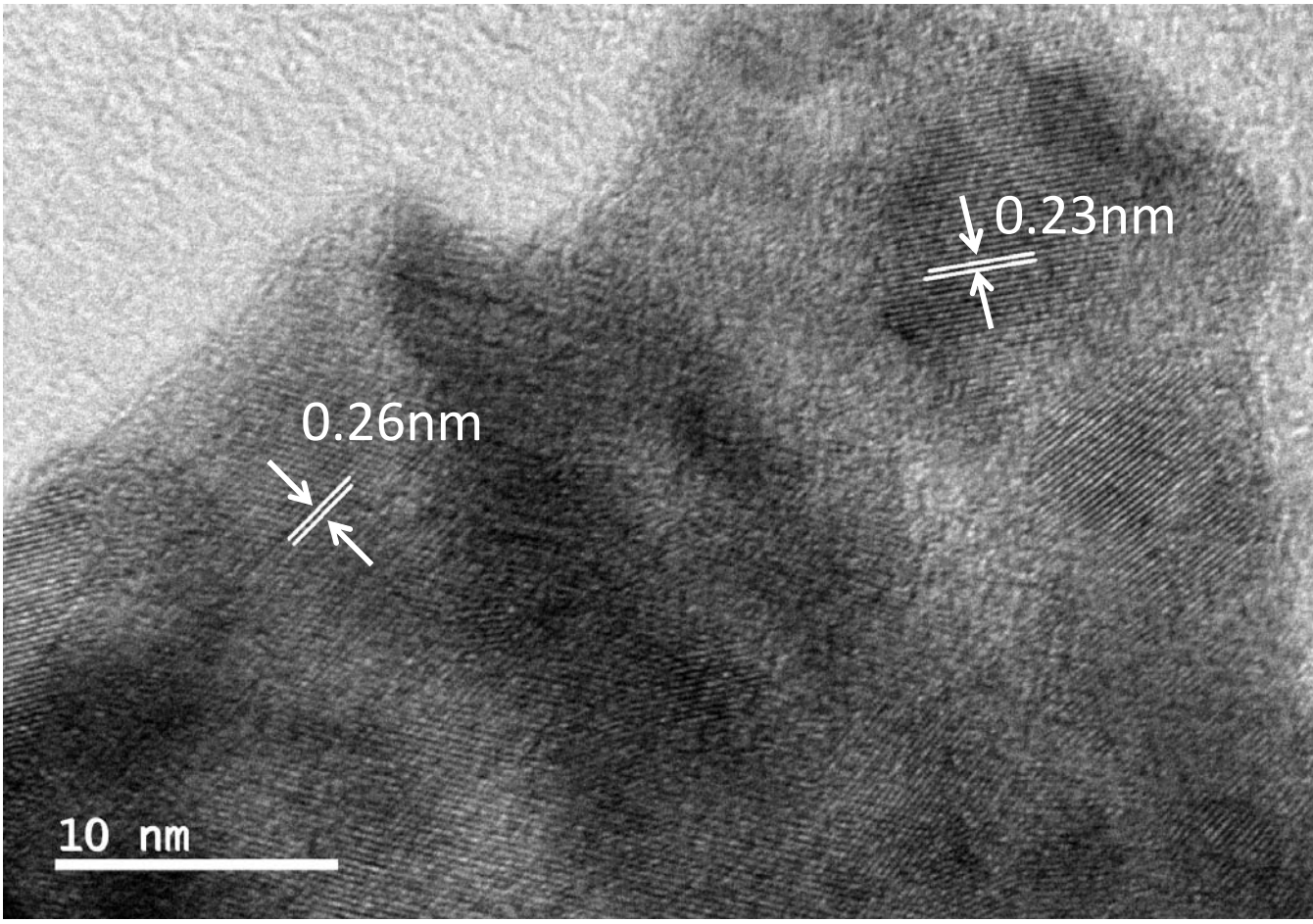
Table Captions

Table 1 Summary of normalized reaction rate constants and deactivation rates on Mo_2C and Pd/SiO_2 for the hydrogenation of dienes

Table 2 Selectivity comparison of supported Pd and Ni catalysts with Mo_2C and Ni/Mo_2C catalysts

Table 3 Cost evaluation of Pd/SiO_2, Mo_2C and 8.6%Ni/Mo_2C for 1,3-butadiene hydrogenation


(a)
(b)
Intensity (a.u.)
(d)
20
40
60
80
2θ (°)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0.26nm
10 nm

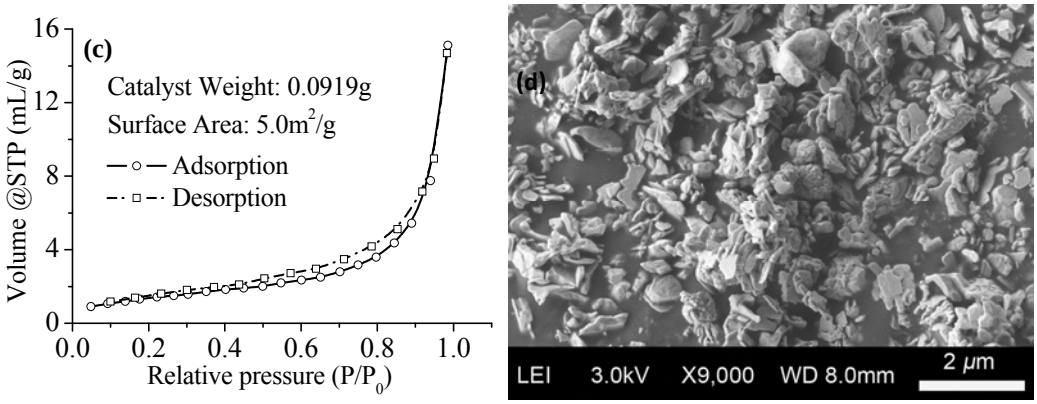

Fig. 1 Characterizations of Mo_2C: (a) XRD; (b) TEM; (c) BET; (d) SEM

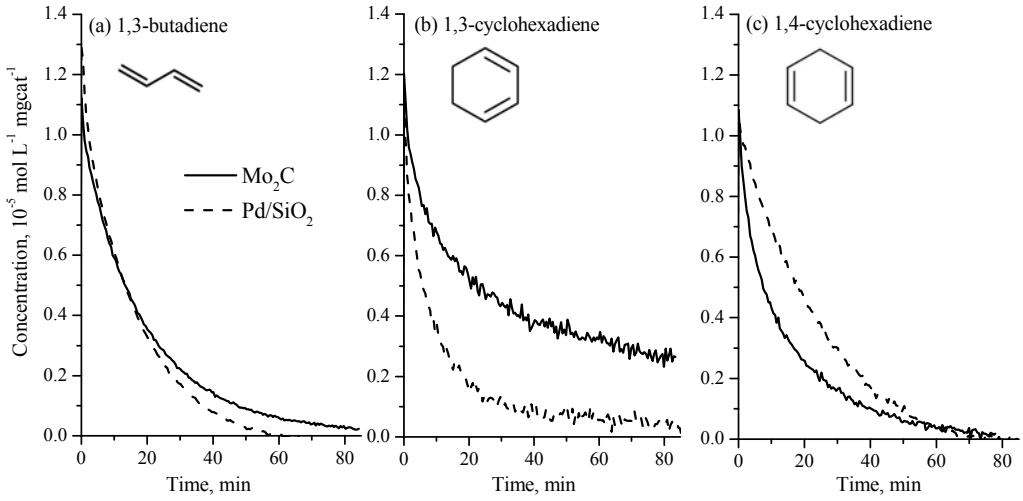

Fig. 2 Consumption rate of (a) 1,3-butadiene (b) 1,3-CHD (c) 1,4-CHD over Mo_2C.(T = 308 K, P_{H2} = 2293 Pa, P_{Diene} = 1040 Pa, and P_{He} = 3333 Pa)

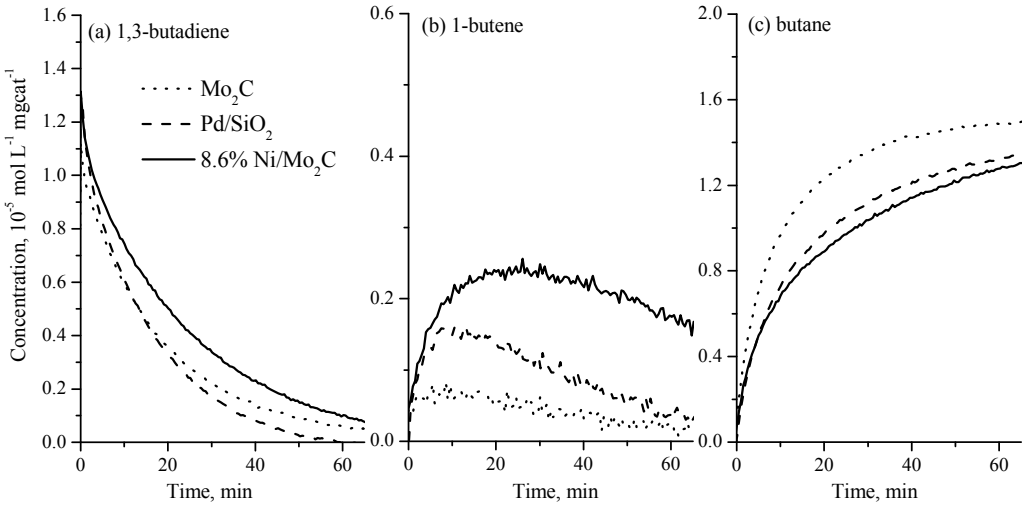

Fig. 3 Consumption rate of (a) 1,3-butadiene and production rates of (b) 1-butene and (c) butane.

(T = 308 K, P_{H2} = 2293 Pa, P_{Diene} = 1040 Pa, and P_{He} = 3333 Pa)

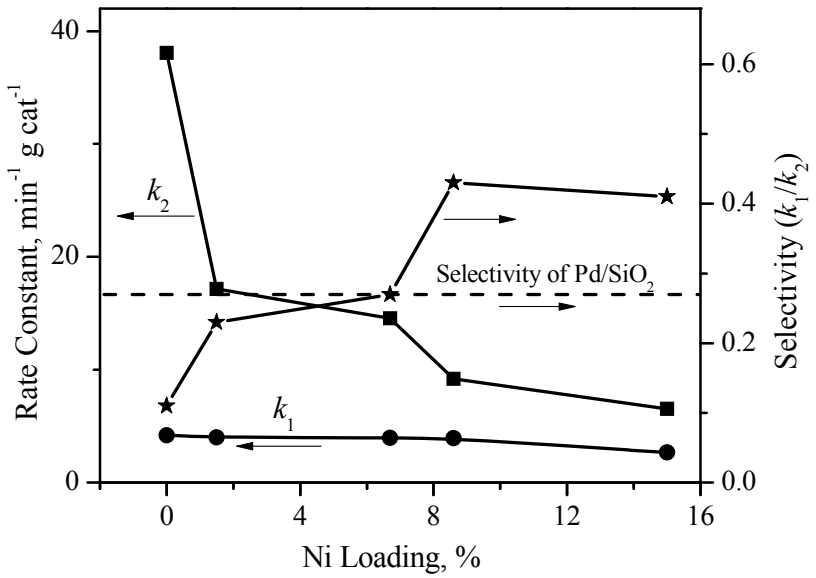

Fig. 4 Normalized reaction rate constants and the estimated selectivity on different loadings of Ni/Mo_2C (k_1: 1,3-butadiene → 1-butene; k_2: 1-butene → butane)

Table 1 Summary of normalized reaction rate constants and deactivation rates on Mo_2C and Pd/SiO_2 for the hydrogenation of dienes

Normalized Rate Constant ($min^{-1}\cdot g\ cat^{-1}$)		1,3-butadiene	1,3-cyclohexadiene	1,4-cyclohexadiene
Pd/SiO_2	k_r	6.1	12.2	3.1
	k_d	0.7	15.5	0
Mo_2C	k_r	5.3	8.6	8.9
	k_d	1.3	18.0	4.9

Table 2 Selectivity comparison of supported Pd and Ni catalysts with Mo_2C and Ni/Mo_2C catalysts

Catalyst	Selectivity (k_1/k_2)
0.9%Pd/SiO_2	0.27
1.5%Ni/SiO_2	0.22
Mo_2C	0.11
8.6%Ni/Mo_2C	0.43

Table 3 Cost evaluation of Pd/SiO_2, Mo_2C and 8.6%Ni/Mo_2C for 1,3-butadiene hydrogenation

Catalyst	Price* ($USD\cdot kg\ cat^{-1}$)	k_1 ($min^{-1}\cdot g\ cat^{-1}$)	α ($10^{-3}\cdot USD\cdot min$)	Selectivity (k_1/k_2)
Pd/SiO_2	216.27	5.6	38.6	0.27
Mo_2C	39.48	4.2	9.4	0.11
8.6%Ni/Mo_2C	38.41	3.9	9.8	0.43

* The prices are from www.metalprice.com