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Preparation and catalytic performance of NiO-MnO₂/Nb₂O₅-TiO₂ for one-step synthesis of 2-ethylhexanol from *n*-butyraldehyde



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ABSTRACT

One-pot synthesis of 2-ethylhexanol(2EHO) from *n*-butyraldehyde is of commercialimportance. The promotion of 2EHO selectivity requires suppressing direct hydrogenation of *n*-butyraldehyde. In this work, a series of NiO- MO_x/Nb_2O_5 -TiO₂ catalysts were prepared and utilized by means of reduction-in-reaction technique, aiming at delaying the formation of metal sites and suppressing the direct hydrogenation. NiO-MnO₂/Nb₂O₅-TiO₂ with a Ni/Mn mass ratio of 10 and NiO-MnO₂ loading of 14.3 wt% shows the best catalytic performance; 2-EHO selectivity could reach 90.0% at a complete conversion of *n*-butyraldehyde. Furthermore the catalyst could be used for four times without a substantial change in its catalytic performance.

1. Introduction

2-Ethylhexanol (2EHO) is an important organic chemical which is mainly used to produce plasticizers such as dioctyl phthalate (DOP), and also used in solvents, defoamers, adhesives, petroleum additives and so on [1,2]. The world's 2EHO production areas are mainly concentrated in the United States, Asia and Western Europe and other countries or regions, accounting for about 85% of the world's total 2EHO production. At present, the 2EHO markets in the United States, Western Europe, and Japan are basically mature, and demand growth will remain at a low level, while demand in Asia and other regions is growing rapidly [3]. The rapid growth of 2EHO breaks the balance of supply and demand in the market. In this context, reducing the production cost of 2EHO is one of the effective ways to improve product competitiveness [4]. The industrial production of 2EHO adopts a low-pressure OXO (hydroformylation) synthesis process consisting of three consecutive steps: propylene hydroformylation to *n*-butyraldehyde, *n*-butyraldehyde selfcondensation to 2-ethyl-2-hexenal (2E2H), and 2E2H hydrogenation to 2EHO [5]. This process suffers from several shortcomings such as long process flow, high energy consumption, large volume emission of alkali wastewater. According to the survey, 30% of the price of 2EHO is spent for purification and wastewater treatment [6]. One-step synthesis of 2EHO from n-butyraldehyde which can simplify the process flow and reduce energy consumption is of industrially importance. In the one-pot synthesis of 2EHO from n-butyraldehyde, the selectivity of 2EHO is governed by the competition between *n*-butyraldehyde selfcondensation and direct hydrogenation. So promoting 2EHO selectivity requires suppressing the direct hydrogenation of *n*-butyraldehyde. Several researchers [7-9] studied this one-pot synthesis using multifunctional supported metal catalysts, but attained unsatisfactory 2EHO selectivity due to rather high direct hydrogenation rate. Fortunately, Zhao [10] obtained a pretty high selectivity of 2-propylheptanol (2PHO) in one-pot synthesis of 2PHO from n-valeraldehyde using a NiO-Co₃O₄/ Nb₂O₅-TiO₂ catalyst by means of reduction-in-reaction technique. By this doing, the formation of metal nickel and cobalt sites is delayed and the direct hydrogenation of *n*-valeraldehyde is suppressed. Speaking in detail, they adjusted the catalyst acidity and basicity by introducing Nb₂O₅ onto TiO₂ to facilitate *n*-valeraldehyde self-condensation. To help the reduction of NiO in the reaction process, a second metal component was added to decrease the reduction temperature of NiO. These successful measures provided a valuable reference for our work. We started with screening a suitable second metal component based on NiO/Nb₂O₅-TiO2 to improve the catalytic performance for one-pot synthesis of 2EHO from *n*-butyraldehyde.

In this work, we will employ this procedure to inhibit the direct hydrogenation of *n*-butyraldehyde and improve the selectivity of 2EHO. A series of NiO-MOx/Nb₂O₅-TiO₂ catalysts were prepared and their catalytic performances were evaluated. The result demonstrated that NiO-MnO₂/Nb₂O₅-TiO₂ catalyst showed excellent performance. The characterization results confirmed a strong interaction between Ni and

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Received 28 July 2020; Received in revised form 10 November 2020; Accepted 17 November 2020 Available online 21 November 2020 1566-7367/© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). Mn which is responsible for the high catalytic activity and stability.

2. Experimental

The catalyst preparation, characterization and catalytic performance evaluation are enclosed in the Supporting Information.

3. Results and discussion

3.1. Effect of second-metal component on the catalytic performance of NiO/Nb₂O₅-TiO₂

The effects of second-metal components on the performance of NiO/ Nb₂O₅-TiO₂ were evaluated and the results are shown in Table S1 in the supporting information. *n*-butyraldehyde was completely converted for all the bimetallic catalysts, suggesting that the addition of the secondmetal components showed no significant effect on the catalytic activity. The selectivity of 2EHO decreased in the following order: Mn > Co > blank>Fe > Ir > Rh > Ru > Pt > Pd, and *n*-butanol selectivity decreased in the following order: Pt > Ru > Ir > Rh > Pd > Fe > blank>Co > Mn. Among the bimetallic catalysts, NiO-MnO₂/Nb₂O₅-TiO₂ showed the best catalytic performance; the selectivity of 2EHO reached 88.5% whereas the selectivity of *n*-butanol was only 11.4%.

In order to further investigate the effect of second-metal component on the reduction property of NiO, XRD tests of the bimetallic catalysts were performed before and after reaction and the results are shown in Fig. S1 in the supporting information. The diffraction peak of NiO at 2θ $= 43.26^{\circ}$ can be detected in the fresh catalyst in addition to the diffraction peaks of anatase TiO₂ at $2\theta = 25.18^{\circ}$, 37.69° , 47.91° , 53.78° , 54.93°, 62.61°, 68.65°, 70.17°, 74.94° and 82.56°. The diffraction peaks of metal Ni can be found at $2\theta=44.59^\circ,\,51.72^\circ$ and 76.33° in the recovered catalysts, indicating that NiO was reduced during the reaction process. However, weak characteristic peaks of NiO can be detected either for the recovered bimetallic catalysts with Ru, Rh, Pd, and Pt as the second-metal component, indicating that NiO was not completely reduced and thus leading to a poor catalytic performance. No characteristic peaks of the second-metal and its metal oxide were detected before and after reaction due to its low concentration, small grain and good dispersion.

For better analyzing the effect of the second-metal component on the physical structure of NiO/Nb₂O₅-TiO₂, N₂ adsoprtion and desorption tests were performed and the results are shown in Table S2 in the supporting information.

For further investigating the effect of the second-metal component Mn on the reduction temperature of NiO in NiO/Nb2O5-TiO2, H2-TPR analyses of NiO/Nb2O5-TiO2 and NiO-MnO2/Nb2O5-TiO2 catalysts were performed and the results are shown in Fig. S2 in the supporting information. For comparison, the H2-TPR profiles of other supported bimetallic oxide catalysts are presented in Figs. S3-S9 and the H2-TPR data are listed in Table S3. There are two reduction peaks in NiO/Nb₂O₅-TiO₂: the peak at 328.5 °C belongs to the reduction of large NiO grains which do not interact with the support, and the peak at 429.5 °C is ascribed to the reduction of NiO grains which interacts with the support [11,12]. NiO-MnO₂/Nb₂O₅-TiO₂ also has two obvious reduction peaks: the peak at 326.3 $^\circ C$ is attributed to both the reduction of MnO_2 \rightarrow Mn₂O₃ and large NiO grains which do not interact with the support while the peak at 403.2 $^\circ C$ belongs to the reduction of both $Mn_3O_4 \rightarrow$ MnO and NiO which interacts with the support [13]. Compared with NiO/Nb2O5-TiO2, the reduction peak of NiO shifts to a lower temperature and the hydrogen consumption of NiO decreases, possibly because the interaction between Ni and Mn weakens the interaction between the metals and the support. Additionally, it is concluded from Figs. S3-S9 and Table S3 that the addition of the second metal component facilitates the reduction of NiO.

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Table 1

Catalytic properties of NiO-MnO_2/Nb_2O_5-TiO_2 with different mass ratios of Ni/ Mn.

	, o SZEZH/	30 32EH/ 30	$S_{2EHO}/\%$
.0 16.6	0	0	77.9
.0 11.4	0	0	88.5
.0 8.8	37.8	43.6	0
.0 10.3	80.6	0	0
.0 12.7	67.9	0	0
.0 2.1	70.4	0	0
	0.0 16.6 0.0 11.4 0.0 8.8 0.0 10.3 0.0 12.7 0.0 2.1	0.0 16.6 0 0.0 11.4 0 0.0 8.8 37.8 0.0 10.3 80.6 0.0 12.7 67.9 0.0 2.1 70.4	0.0 16.6 0 0 0.0 11.4 0 0 0.0 8.8 37.8 43.6 0.0 10.3 80.6 0 0.0 12.7 67.9 0 0.0 2.1 70.4 0

Reaction conditions: a weight percentage of catalyst = 15%, T = 180 °C, P = 4 MPa, t = 6 h.

BA: butanal; BO: butanol; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; 2EHO: 2-ethylhexanol. *X*: conversion; *S*: selectivity.

3.2. Effect of preparation conditions of NiO-MnO₂/Nb₂O₅-TiO₂

3.2.1. Influence of Ni/Mn mass ratio

The influence of Ni/Mn mass ratio on the catalytic performance of NiO-MnO₂/Nb₂O₅-TiO₂ was investigated and the results are shown in Table 1. *n*-Butyraldehyde achieved a complete conversion within the range of Ni/Mn mass ratio investigated, suggesting that Ni/Mn mass ratio shows insignificant influence on the catalytic activity. As Ni/Mn mass ratio decreases, the selectivity of 2EHO increases first, reaches its optimum at a Ni/Mn mass ratio of 10: 1 and then decreases suddenly to 0. We suppose that excessive amount of MnO₂ will ruin the hydrogenation activity of NiO-MnO₂/Nb₂O₅-TiO₂ catalyst by covering the sites of metal Ni. The coverage of the sites of metal Ni by Mn will destroy the hydrogenation activity of the catalyst definitely and cause the formation of 2E2H (C=C bond and C=O bond are left) and 2EH (C=O bond is left) instead of 2EHO, as entry 3 of Table 1 showed. Therefore, the suitable Ni/Mn mass ratio is determined to be 10: 1.

In order to further analyze the influence of Ni/Mn mass ratio on the catalytic performance of NiO-MnO2/Nb2O5-TiO2, the XPS analyses of Ni 2p and Mn 2p were carried out. The XPS spectra are shown in Fig. S10 and the binding energy data are listed in Table S4 and Table S5. According to literatures [10,14,15], the binding energies of Ni $2p_{3/2}$ of Ni^{2+} are 853.1 eV and 856.1 eV; the binding energy of Ni $2p_{1/2}$ of Ni^{2+} are 863 eV and 873 eV; the binding energies of Mn $2p_{3/2}$ of Mn⁴⁺ is 642.01 eV; the binding energy of Mn $2p_{1/2}$ of Mn⁴⁺ is 653.7 eV; the binding energies of Mn $2p_{3/2}$ of Mn²⁺ is 641.2 eV, and the satellite of MnO is 646.4 eV; the binding energy of Mn $2p_{1/2}$ of Mn²⁺ is 652.8 eV; the binding energy of pure metal Ni is 852.4 eV; and the binding energy of pure metal Mn is 640.1 eV. It is demonstrated from the binding energy data of Ni 2p and Mn 2p in Table S4 that the valence state of Ni and Mn elements in the fresh catalysts separately is Ni²⁺ and Mn⁴⁺ and their corresponding metal compounds are respectively NiO and MnO₂. It is found from the binding energy data in Table S5 that the Ni 2p_{3/2} binding energy of metal Ni in the recovered catalysts is less than that of the pure metal Ni while the $\text{Mn}2p_{3/2}$ binding energy of metal Mn in the recovered catalysts is greater than that of the pure metal Mn. So this demonstrates that there is an interaction between Ni and Mn and thus a Ni-Mn alloy possibly forms. In addition, the characteristic peaks of NiO, MnO and MnO₂ can also be detected in the XPS spectra of the spent catalysts due to the oxidation of the surface metals Ni and Mn in the air during the analysis process.

For a further verification of the existence of interaction between Ni and Mn and a Ni—Mn alloy, XRD pattern of NiO-MnO₂/Nb₂O₅-TiO₂ catalyst with a Ni/Mn mass ratio of 10:1 was recorded and the result is showed in Fig. S11. It can be seen that an obvious diffraction peak can be detected around 44.6°, which is between 44.507° of pure metal Ni (111) crystal plane and 44.785° of pure metal Mn (222) crystal plane, indicating that Ni—Mn alloy is formed. In order to determine the distribution of metal Ni and Mn, EDS mapping was measured and the results are illustrated in Fig. S12. The EDS mapping showed that metal Ni and Mn were well-dispersed within the catalyst grain. TEM-EDS line scan Table 2

Catalytic properties of NiO-MnO₂/Nb₂O₅-TiO₂ with different NiO-MnO₂ loading.

Loading of NiO-MnO $_2$ /%	Loading of NiO/%	Loading of MnO ₂ /%	$X_{\rm BA}$ /%	$S_{\rm BO}/\%$	S _{2E2H} /%	S _{2EH} /%	$S_{2 \mathrm{EHO}} / \%$
8.7	7.7	1.0	100.0	10.9	0	3.7	79.4
11.5	10.2	1.3	100.0	11.7	0	0	83.9
14.3	12.7	1.6	100.0	11.4	0	0	88.5
17.2	15.3	1.9	100.0	13.8	0	0	81.7
20.0	17.8	2.2	100.0	13.5	0	0	81.4

Reaction conditions: a weight percentage of catalyst = 15%, T = 180 °C, P = 4 MPa, t = 6 h.

BA: butanal; BO: butanol; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; 2EHO: 2-ethylhexanol. X: conversion; S: selectivity.

 Table 3

 Effect of reaction conditions on one-pot synthesis of 2EHO from *n*-butyraldehyde.

Catalyst amount/ wt%	Reaction temperature/ °C	Reaction time/h	Reaction pressure/ MPa	S _{BO} / %	S _{2EH} / %	S _{2EHO} / %
12.5	180	6	4	13.6	3.9	77.3
15.0	180	6	4	11.4	0	88.5
17.5	180	6	4	10.6	0	88.2
20.0	180	6	4	12.1	12.3	75.8
15	180	6	4	11.4	0	88.5
15	190	6	4	10.1	0	89.3
15	200	6	4	9.3	0	90.4
15	210	6	4	8.5	0	90.8
15	220	6	4	6.6	0	91.0
15	230	6	4	5.5	0	90.8
15	200	4	4	11.0	24.8	59.2
15	200	5	4	9.9	0	90.0
15	200	6	4	9.3	0	90.4
15	200	7	4	9.8	0	89.4
15	200	6	3	7.7	40.4	53.5
15	200	6	4	9.3	0	90.4
15	200	6	5	12.0	0	85.4

n-butyraldehyde conversion was 100% and 2-ethyl-2-hexenal selectivity was 0 at all reaction conditions. BO: *n*-butanol; 2EH: 2-ethylhexanal; 2EHO: 2-ethylhexanol. *S*: selectivity.

analysis on a single NiO-MnO₂/Nb₂O₅-TiO₂ catalyst grain (Fig. S13) showed that the signal intensity patterns of Ni and Mn are similar and closely related to each other. This observation proves a good distribution of Ni and Mn and also suggests a possible formation of Ni—Mn alloy.

For explaining the difference in the catalytic performance of the catalysts with different Ni/Mn mass ratios, we calculated the "the number of holes in d-orbital" of each catalyst. According to the energy band theory, when the number of holes in d-orbital is approximately equal to the coordination number of electron transfer required by the reactant molecules, the chemical adsorption is moderate and a higher catalytic activity will be shown [16]. For a hydrogenation reaction, the electron transfer number is 1 when hydrogen is adsorbed on the metal surface. So the closer to 1 the number of holes in d-orbital of catalysts, the better the catalytic performance. It can be seen from Table S5 that the number of holes in d-orbital is closest to 1 when the Ni/Mn mass ratio is 10. Thus the catalytic performance is the best in this case, being consistent with the data in Table 1.

3.2.2. Influence of NiO-MnO₂ loading

The influence of NiO-MnO₂ loading on the catalytic performance of NiO-MnO₂/Nb₂O₅-TiO₂ was investigated and the results are shown in Table 2. With an increase in the loading of NiO-MnO₂, *n*-butyraldehyde can be completely converted, the selectivity of 2EHO first increases and then decreases while the selectivity of *n*-butanol first decreases and then increases. NiO-MnO₂/Nb₂O₅-TiO₂ with the loading of NiO-MnO₂ of 14.3 wt% shows the best catalytic performance; the highest selectivity of 2EHO of 88.5% and the lowest selectivity of *n*-butanol of 11.4% are attained. Therefore, the suitable NiO-MnO₂ loading is determined to be 14.3 wt%.

3.3.	Effect o	of reaction	conditions of	n one-step	synthesis	of 2EHO	from n-
buty	raldehyd	le					

The reaction conditions have an important influence on the catalytic performance. Therefore, in order to improve the catalytic performance of NiO-MnO₂/Nb₂O₅-TiO₂ and to lay the foundation for the kinetic experimental study, the influence of the reaction conditions was investigated and the results are shown in Table 3. n-Butyraldehyde was completely converted at the reaction conditions inspected, suggesting a high catalytic activity of NiO-MnO2/Nb2O5-TiO2. With an increase of catalyst amount, the selectivity of 2EHO first increased, reached its highest (88.5%) at a weight percentage of catalyst of 15.0 wt% and then remained unchanged while the selectivity of n-butanol first decreased and then remained unchanged. With an increase of temperature, the selectivity of 2EHO firstly increased and then leveled off while the selectivity of n-butanol gradually decreased. In addition, 2EHO selectivity decreased significantly at a temperature higher than 220 °C, accompanied by the increase of selectivity of some side-products such as butyl butyrate, octyl butyrate and other ester by-products. This demonstrates that high reaction temperature favors esterification reaction which consumes n-butanol and 2EHO and thus decreases the total selectivity of n-butanol and 2EHO. The selectivity of 2EHO first increased and then decreased while the selectivity of *n*-butanol gradually increased as the reaction pressure increases. When the reaction pressure is less than 4 MPa, the hydrogen pressure is so low that the hydrogenation is not complete and the reaction products are mainly 2EH. When the reaction pressure is greater than 4 MPa, 2EHO selectivity decreases and n-butanol selectivity increases with the increase of reaction pressure. This indicates that an overhigh reaction pressure accelerates the reduction of NiO-MnO2 and exposes the metal site Ni-Mn too soon, facilitating the direct hydrogenation of *n*-butyraldehyde and thus reducing 2EHO selectivity. The selectivity of 2EHO increased first and then leveled off while the selectivity of n-butanol decreased first and then leveled off when the reaction time was prolonged. The selectivity of 2EHO is only 24.8% at a reaction time less than 5 h, indicating an incomplete C=O bond hydrogenation. However, the selectivity of nbutanol and 2EHO remained basically unchanged at a reaction time longer than 5 h.

3.4. Reusability of NiO-MnO₂/Nb₂O₅-TiO₂

After the reaction, the catalyst was recovered and washed with ethanol several times, dried at 100 °C for 12 h and then calcined at 450 °C for 2 h before reused in the next cycle. The reusability of the catalyst was investigated under the suitable reaction conditions and the results are shown in Table S6. The catalytic performance of the catalyst did not change significantly after reuse for 4 times, indicating that NiO-MnO₂/Nb₂O₅-TiO₂ has a good reusability.

4. Conclusion

In order to increase 2EHO selectivity in the one-pot reaction of *n*butyraldehyde self-condensation and hydrogenation, a NiO-MnO₂/ Nb₂O₅-TiO₂ catalyst was prepared. The reduction-in-reaction technique was employed to delay the formation of metal sites and to suppress *n*butyraldehyde direct hydrogenation. The suitable Ni/Mn mass ratio and NiO-MnO₂ loading are separately 10 and 14.3 wt%. The XPS analysis results showed there is an interaction between Ni and Mn. The selectivity of 2EHO reached 90.0% at a 100.0% of *n*-butyraldehyde conversion under the suitable reaction conditions. The catalyst could be used for four times without a substantial change in its catalytic performance, indicating that this catalyst has a good stability.

CRediT authorship contribution statement

Sibo Li: Writing - original draft, Validation, Investigation. Jiaxun Zhang: Conceptualization, Validation, Formal analysis, Investigation, Writing - original draft, Methodology. Hualiang An: Resources, Writing - review & editing, Project administration. Xinqiang Zhao: Resources, Writing - review & editing, Funding acquisition, Supervision, Project administration. Yanji Wang: Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106250.

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