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Short communication

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# Effect of second metal component on the reduction property and catalytic performance of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> for direct synthesis of 2-propylhep-tanol from *n*-valeraldehyde

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Keywords: n-Valeraldehyde 2-Propylheptanol Direct synthesis NiO-Co <sub>3</sub> O <sub>4</sub> /Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	In order to improve the catalytic performance of NiO/Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> , several kinds of the second metal oxide component $MO_x$ (M = Pd, Co, Ir or Rh) were separately introduced and their effects on the reduction property and catalytic performance were evaluated. The results showed that the reduction temperature of NiO decreased and NiO-Co <sub>3</sub> O <sub>4</sub> /Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> exhibited the best catalytic performance. The reason for the enhancement of NiO reducibility may stem from the interaction of M with Ni and the hydrogen spillover as confirmed by various characterization techniques including XRD, H <sub>2</sub> -TPR, H <sub>2</sub> -TPD and XPS.

# 1. Introduction

2-Propylheptanol (2-PH) is an important plasticizer alcohol. By comparison with the traditional dioctyl phthalate (DOP) plasticizer produced by 2-ethylhexanol, 2-PH-derived plasticizers such as 2-propylheptyl phthalate (DPHP) are more environmentally friendly due to their temperature resistance, lower volatility, and being nontoxic and so on [1]. The industrial production of 2-PH mainly includes three reaction steps: hydroformylation of butene, self-condensation of *n*-valeraldehyde, and hydrogenation of 2-propyl-2-heptenal. If *n*-valeraldehyde self-condensation and 2-propyl-2-heptenal hydrogenation can be integrated, that is, direct synthesis of 2-PH from *n*-valeraldehyde, the process will be simplified and the energy consumption will be reduced, thus the cost of production being lowered. Therefore, the investigation on this reaction integration is of a crucial significance for both academic research and industrial production of 2-PH.

At present, a few studies about the direct synthesis of 2-PH from *n*-valeraldehyde have been reported. Sharma and Jasra [2] employed Ru-HT (ruthenium hydrotalcite) bifunctional catalyst for single pot synthesis of 2-PH from *n*-valeraldehyde and obtained a 2-PH selectivity of only 48%. In our previous work [3], the catalytic performances of Ni/TiO<sub>2</sub>, Ni/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, and NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts for the direct synthesis of 2-PH from *n*-valeraldehyde were separately evaluated. The results showed that the introduction of Nb<sub>2</sub>O<sub>5</sub> could effectively tune the

acidity and basicity on the Ni/TiO<sub>2</sub> surface and NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst could delay the formation of metal sites so as to suppress the direct hydrogenation of *n*-valeraldehyde. However, the formation of a majority of incompletely hydrogenated products suggested that NiO was not completely reduced in reaction. To facilitate the complete reduction of NiO in reaction, a second-metal component was introduced into NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst to lower the reduction temperature of NiO.

The effect of a second-metal component on the reduction property and the catalytic performance of Ni-based catalysts has been reported. Lock et al. [4] investigated the effect of Pd addition on the catalytic performance of Ni/Al<sub>2</sub>O<sub>3</sub> for methane decomposition and found that adding Pd into Ni/Al2O3 catalyst improved the catalytic activity and inhibited carbon deposition. The H2-TPR characterization result showed that the reduction temperature of NiO-PdO/Al2O3 catalyst shifted to a lower temperature, indicating that the addition of Pd promoted the reduction of NiO. Lin et al. [5] studied the effect of Ir addition on the catalytic performance of Ni/TiO2 for hydrogenation of cinnamaldehyde and found that adding Ir into Ni/TiO2 improved the catalytic performance and stability. The results of H2-TPR, H2-TPD and XPS analyses showed that the interaction between Ni and Ir could lower the reduction temperature of NiO. Andonova et al. [6] compared the catalytic performance of Ni-Co/Al<sub>2</sub>O<sub>3</sub> with Ni/Al<sub>2</sub>O<sub>3</sub> for hydrogen production from ethanol steam reforming and found that Ni-Co/Al2O3 exhibited better stability and hydrogen selectivity. Compared with the single metal

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Received 11 August 2020; Received in revised form 29 September 2020; Accepted 21 October 2020 Available online 24 October 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/). system, the reduction temperature of NiO decreased and furthermore the reducibility of NiO increased with the increase of Co content. Hou et al. [7] found that Ni/Al<sub>2</sub>O<sub>3</sub> catalyst had good catalytic activity in methane reforming but the catalyst suffered from the problem of deactivation. After introducing a small amount of Rh, the catalytic stability of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was improved. The characterization result showed that Rh improved the dispersion of Ni and decreased the reduction temperature of NiO. In conclusion, adding a second-metal component into Ni-based catalysts can not only improve the catalytic activity and stability, but also reduce the reduction temperature of NiO.

Consequently, a second-metal oxide component  $MO_x$  (PdO,  $Co_3O_4$ ,  $IrO_2$  or  $Rh_2O_3$ ) was introduced into  $NiO/Nb_2O_5$ - $TiO_2$  catalyst to assist NiO reduction in reaction in this work. We aimed to clarify the reason why adding second-metal component could promote the reduction of NiO in the reaction process. So the effect of the addition of a second metal component on the catalytic performance of  $NiO/Nb_2O_5$ - $TiO_2$  was evaluated first and then the effect on the reduction property was analyzed by a series of characterization techniques.

# 2. Experimental

#### 2.1. Catalyst preparation and characterization

NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts were prepared by co-impregnation method. The as-prepared samples were characterized by several techniques, namely, XRD, H<sub>2</sub>-TPR, H<sub>2</sub>-TPD and XPS. More details about the synthesis procedure and characterization can be found in the Supplementary material.

#### 2.2. Catalytic performance evaluation

The catalytic tests were carried out in a 100 mL stainless steel autoclave charged with 3.6 g catalyst and 30 mL (24 g) of *n*-valeraldehyde. Prior to experiments, the air inside was replaced with hydrogen. The mixture was heated and the reaction was carried out at 200 °C for 6 h under the H<sub>2</sub> pressure of 3.0 MPa with stirring. After the completion of reaction, the mixture was cooled to room temperature and was separated by centrifugation. The liquid was quantitatively analyzed by a SP-2100 gas chromatograph (Beijing Beifen-Ruili Analytical Instrument Co., Ltd) equipped with a flame ionization detector (FID) operated at 250 °C according to the literature [1].

#### 3. Results and discussion

# 3.1. Effect of MO<sub>x</sub> on catalytic performance of NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>

The effect of second-metal component on the catalytic performance of NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> was evaluated and the results are shown in Table 1. It can be seen that *n*-valeraldehyde was incompletely converted and the target product 2-PH was not formed over NiO/Nb2O5-TiO2 catalyst. Some intermediates (2-propyl-2-heptenal and 2-propylheptanal) and a small amount of direct hydrogenation product n-pentanol were formed instead, indicating that NiO failed to be completely reduced in reaction. However, n-valeraldehyde was completely converted and 2-PH became the main product over NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts, suggesting that NiO could be reduced in reaction. It can also be seen that the ratio of S2-PH to  $S_{PO}$  was 0 and the selectivity of *n*-pentanol was only 3.2% over NiO/Nb2O5-TiO2 catalyst, indicating that n-valeraldehyde selfcondensation reaction took place predominately while hydrogenation reaction hardly occurred. The ratio of S<sub>2-PH</sub> to S<sub>PO</sub> varied with different bimetallic catalysts and decreased as following order: NiO-Co<sub>3</sub>O<sub>4</sub>/  $Nb_2O_5\text{-}TiO_2 > NiO\text{-}PdO/Nb_2O_5\text{-}TiO_2 > NiO\text{-}IrO_2/Nb_2O_5\text{-}TiO_2 > NiO\text{-}$ Rh<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>. If the ratio of S<sub>2-PH</sub> to S<sub>PO</sub> is 1, the competitiveness of n-valeraldehyde self-condensation reaction is comparable with respect to that of n-valeraldehyde direct hydrogenation reaction. If the ratio of S2-PH to SPO is greater than 1, n-valeraldehyde self-condensation

# Table 1

Effect of MO<sub>x</sub> on catalytic performance of NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.

Catalyst	X <sub>V</sub> / %	S <sub>PO</sub> / %	S₂. <sub>РНА</sub> ∕ %	S <sub>2-</sub> phea/ %	S <sub>2-</sub> <sub>РН</sub> / %	S <sub>2-</sub> <sub>РН</sub> / S <sub>PO</sub>	Period of instantaneous hydrogen flow time/min
NiO/ Nb <sub>2</sub> O <sub>5</sub> - TiO <sub>2</sub> <sup>a</sup>	93.1	3.2	39.6	56.0	0	0	None
NiO- PdO/ Nb <sub>2</sub> O <sub>5</sub> - TiO <sub>2</sub>	100	23.0	2.3	0	61.3	2.7	0–45.4
NiO- Co <sub>3</sub> O <sub>4</sub> / Nb <sub>2</sub> O <sub>5</sub> - TiO <sub>2</sub>	100	21.8	0	0	77.1	3.5	52.5–118.8
NiO- IrO <sub>2</sub> / Nb <sub>2</sub> O <sub>5</sub> - TiO <sub>2</sub>	100	28.9	0	0	64.8	2.2	9–106.3
NiO- Rh <sub>2</sub> O <sub>3</sub> / Nb <sub>2</sub> O <sub>5</sub> - TiO <sub>2</sub>	100	33.9	0	0	61.7	1.8	0–94
Co <sub>3</sub> O <sub>4</sub> / Nb <sub>2</sub> O <sub>5</sub> - TiO <sub>2</sub> <sup>b</sup>	100	20.6	24.1	23.1	13.0	0.6	None

V: *n*-valeraldehyde; PO: *n*-pentanol; 2-PHA: 2-propylheptanal; 2-PHEA: 2-propyl-2-heptenal;

2-PH: 2-propylheptanol. X: conversion; S: selectivity.

Reaction conditions: a weight percentage of catalyst =15%, T = 200 °C, P = 3 MPa, t = 6 h.

 $\rm Nb_2O_5$  loading was 5 wt% of TiO\_2, NiO loading was 13 wt% of  $\rm Nb_2O_5\text{-}TiO_2$  and MO\_x loading was 1 wt% of Nb\_2O\_5\text{-}TiO\_2.

<sup>a</sup> NiO loading was 14 wt% of Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.

<sup>b</sup> Co<sub>3</sub>O<sub>4</sub> loading was 14 wt% of Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.

reaction is more competitive than *n*-valeraldehyde direct hydrogenation reaction. In this work, the ratio of  $S_{2.PH}$  to  $S_{PO}$  was greater than 1 over NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts. Furthermore, the ratio of  $S_{2.PH}$  to  $S_{PO}$  was the largest, up to 3.5 over NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst; the selectivity of 2-PH reached 77.1% while the selectivity of *n*-pentanol was only 21.8%. Therefore, NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst was chosen as the suitable bimetallic catalyst for further research.

In order to analyze the reason why the NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst has excellent catalytic performance, the catalytic performance of Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> was evaluated under the same conditions as NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and the results were also listed in Table 1. The condensation product was not completely hydrogenated, indicating that a lower hydrogenation activity over Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst. It also showed that there was interaction between Ni and Co, which affected the catalytic performance of NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.

The above results showed that adding second-metal component could promote the reduction of NiO in the reaction process. To analyze the promotion effect of a second-metal component on NiO reduction and on the catalytic performance of NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts were characterized by means of XRD, H<sub>2</sub>-TPR, H<sub>2</sub>-TPD and XPS techniques.

#### 3.2. Characterization of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts

#### 3.2.1. Analysis of XRD

XRD patterns of the fresh and the recovered NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts are shown in Fig. 1. NiO were detected besides anatase TiO<sub>2</sub> in the fresh NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts. However, the characteristic peaks of Nb<sub>2</sub>O<sub>5</sub>, PdO, IrO<sub>2</sub>, Rh<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> were not observed due to their low loading, smaller grain size and high dispersion on the supporter surface. For the recovered NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, a weak diffraction peak of NiO was detected besides



Fig. 1. XRD patterns of different catalysts before and after reaction 1: NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>; 2: NiO-PdO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>; 3: NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>; 4: NiO-IrO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>; 5: NiO-Rh<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.

\*: fresh; #: recovered.  $\bullet$ : NiO;  $\blacklozenge$ : Ni<sup>0</sup>.

metallic nickel, indicating that NiO was incompletely reduced in the reaction process. However, NiO was not detected while an obvious diffraction peak of Ni was detected in the recovered NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, indicating that adding MO<sub>x</sub> could indeed promote the reduction of NiO in reaction process, which was consistent with the activity evaluation results.

# 3.2.2. Analysis of H<sub>2</sub>-TPR

H<sub>2</sub>-TPR analyses of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (M = Pd, Ir, Rh or Co) were made and their profiles are shown in Fig. 2 while the measurement data is listed in Table S1 in the Supplementary material. As to NiO-PdO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, there were four hydrogen consumption peaks separately at 72.2 °C, 235.0 °C, 306.7 °C and 419.1 °C. The weak peak at 72.2 °C was ascribed to the reduction of PdO. The peak at 235.0 °C was ascribed to the reduction of PdO. The peak at 306.7 °C was ascribed to the reduction of NiO strongly interacted with PdO and the Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface [8]. The peak at 419.1 °C was ascribed to the reduction peaks at 419.1 °C was ascribed to the reduction peak at 419.1 °C was ascribed to the reduction for NiO strongly interacted with PdO and the Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface [8]. The peak at 419.1 °C was ascribed to the reduction peak of NiO interacted with the Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface. NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst had four hydrogen consumption peaks separately at 262.2 °C, 302.1 °C, 364.7 °C and 399.2 °C. The peak at 262.2 °C and Ni<sup>2+</sup> to Ni<sup>0</sup> while the peak at 364.7 °C and 399.2 °C should



Fig. 2. H<sub>2</sub>-TPR curves of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts.

be attributed to the reduction of both  $\text{Co}^{2+}$  to  $\text{Co}^{0}$  and the reduction of Ni<sup>2+</sup> strongly interacted with the Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface [9]. NiO-IrO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst had four hydrogen consumption peaks separately at 163.5 °C, 220.6 °C, 299.2 °C and 409.1 °C, being ascribed to the reduction of IrO<sub>2</sub> with large grains, IrO<sub>2</sub>-NiO, NiO strongly interacted with IrO<sub>2</sub> and the Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface, and NiO interacted with Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> [5]. NiO-Rh<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst had four hydrogen consumption peaks at 81.5 °C, 254.6 °C, 288.8 °C and 401.2 °C, being separately ascribed to the reduction peaks of Rh<sub>2</sub>O<sub>3</sub> with large grains, Rh<sub>2</sub>O<sub>3</sub>-NiO, NiO strongly interacted with Rh<sub>2</sub>O<sub>3</sub> and the Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> surface, and NiO interacted [10].

In the case of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (M = Pd, Ir, Rh or Co) catalysts, the main reduction peaks appeared at lower temperatures compared with that of NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>. More specifically, the reduction peak of NiO shifted to lower temperatures after the addition of PdO, IrO<sub>2</sub>, Rh<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> into NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, indicating that the reduction of NiO was promoted. This promoting effect is due to the hydrogen spillover and the dissociated hydrogen species which can move from the metals (M = Pd, Ir, Rh or Co) to the surface of NiO [9,11,12]. Moreover, according to the work of Xiang et al. [11], the simultaneous reduction of Ni and Co species would benefit the formation of Ni—Co alloy phase and that the formation of Ni—Co alloy phase could facilitate the reduction process. Therefore, we speculate the interaction between Ni and Co and the formation of Ni—Co alloy in the catalyst reduction process.

The above analyses showed that the interaction between Ni and M (M = Pd, Co, Ir or Rh) was the main reason for the shift in the reduction peak of NiO to lower temperatures in NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts. In addition, it can also be seen from Fig. 2 that the reduction peak temperature and hydrogen uptake varied with the kind of the metals added. The order of hydrogen uptake at higher temperature decreased as the following order: NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> > NiO-IrO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> > NiO-PdO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> > NiO-Rh<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, in accordance with the order of total yield of products (2-PH and 2-propylheptanal) in Table 1. This indicates that the more the hydrogen uptake at higher temperature, the more difficult it is to be reduced in reaction, the more advantageous it is to improve the competitiveness of *n*-valeraldehyde self-condensation and then the selectivity of 2-PH.

#### 3.2.3. Analysis of H<sub>2</sub>-TPD

NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> were reduced firstly and then characterized by H<sub>2</sub>-TPD. The profiles are shown in Fig. S1 while the measurement data is summarized in Table 2. It can be seen that Ni-M/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts had different desorption peak temperature and different hydrogen desorption amount with respect to different M. The top

#### Table 2

H<sub>2</sub>-TPD analysis data of different bimetallic catalysts.

Catalyst	$H_2$ desorption peak at lo	ower temperature	$H_2$ desorption peak at h	Total H <sub>2</sub> desorption amount/	
	Top temperature/°C	$H_2$ desorption amount/ $\mu mol \cdot g^{-1}$	Top temperature/°C	$H_2$ desorption amount/ $\mu mol \cdot g^{-1}$	µmol·g <sup>-1</sup>
Ni/Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	_	_	426.7	18.4	18.4
Ni-Pd/Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	226.6	61.7	_	_	61.7
Ni-Co/Nb2O5-TiO2	246.4	31.5	_	-	31.5
Ni-Ir/Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	195.7	71.3	-	_	71.3
Ni-Rh/Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub>	184.0	84.9	-	-	84.9

temperature of hydrogen desorption peak increased in the following order: Ni-Rh/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (184.0 °C) < Ni-Ir/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (195.7 °C) < Ni-Pd/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (226.6 °C) < Ni-Co/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (246.4 °C) < Ni/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (426.7 °C). The hydrogen desorption peak area decreased in the following order: Ni-Rh/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> > Ni-Ir/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> > Ni-Pd/  $Nb_2O_5$ -Ti $O_2 > Ni$ -Co/Nb<sub>2</sub>O<sub>5</sub>-Ti $O_2 > Ni/Nb_2O_5$ -Ti $O_2$ . The top temperature of hydrogen desorption peak of Ni-M/Nb2O5-TiO2 catalysts was lower than that of Ni/Nb2O5-TiO2 catalyst while the hydrogen desorption peak area of Ni-M/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts was larger than that of Ni/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, indicating that the interaction between metal sites and hydrogen was weak and the number of metal sites was more over Ni-M/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts. This suggested that adding the second metal component increased the number of metal sites and promoted hydrogen spillover. In addition, hydrogen spillover was beneficial to the migration of hydrogen species adsorbed on the catalyst surface and to the decrease of reduction temperature of NiO.

It can be seen from Table 1 that the hydrogenation activities of Ni-M/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts (except for NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>) were significantly improved and the instantaneous hydrogen flow could be observed at the beginning of the reaction, resulting in higher yield of *n*-pentanol. This result was ascribed to lower top temperature of hydrogen desorption peak and larger hydrogen desorption amount over Ni-M/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts in H<sub>2</sub>-TPD measurement. However, as for Ni-Co/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, the hydrogen desorption amount was smaller and the top temperature of hydrogen desorption peak was higher than other Ni-M/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts, indicating that the metal active sites on Ni-Co/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst were less and the interaction between hydrogen and the metal active sites was stronger, so a higher temperature was required for hydrogen desorption. This may be the main reason for a relatively low initial hydrogenation activity of NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst compared with other NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts. Fortunately, the low initial hydrogenation activity restrained *n*-valeraldehyde direct hydrogenation and favored the *n*-valeraldehyde selfcondensation.

#### 3.2.4. Analysis of XPS

To further analyze the interaction between Ni and M (M = Pd, Ir, Co or Rh), the chemical environment and the chemical states of Ni and M were investigated by XPS analysis. Fig. 3 displays Ni 2p spectra of the NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst before and after reaction. It can be seen that the binding energies of Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$  in the fresh NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst were respectively 855.3 eV and 873.0 eV, which were ascribed to NiO [12]. Besides the binding energy of NiO, the binding energy of Ni<sup>0</sup> was 852.4 eV in the recovered NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst [13], and the peak intensity was rather weak due to both the incomplete reduction of NiO in the reaction process and the reoxidation of the surface metallic nickel by contacting air in the analysis process.

Subsequently, Fig. 4 respectively displays the spectra of Ni 2p, Pd 3d, Co 2p, Ir 4f and Rh 3d in the NiO- $MO_x/Nb_2O_5$ -TiO<sub>2</sub> catalysts before and after reaction. In the Ni 2p spectra of the fresh NiO- $MO_x/Nb_2O_5$ -TiO<sub>2</sub> catalysts, the characteristic peaks of NiO can be observed besides that of PdO, IrO<sub>2</sub>, Rh<sub>2</sub>O<sub>3</sub> or Co<sub>3</sub>O<sub>4</sub>. In the Ni 2p spectra of the recovered NiO- $MO_x/Nb_2O_5$ -TiO<sub>2</sub> catalysts, the characteristic peaks of Ni<sup>0</sup> can be obviously observed. Moreover, the binding energy of Ni 2p<sub>3/2</sub> of Ni<sup>0</sup> is



Fig. 3. Ni 2p XPS spectra of NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> before and after reaction.

respectively 851.9 eV, 852.2 eV, 852.1 eV and 852.2 eV with respect to different M (M = Pd, Co, Ir and Rh), respectively shifting 0.5 eV, 0.2 eV, 0.3 eV and 0.2 eV to a low binding energy in comparison with the binding energy of Ni<sup>0</sup> in the recovered NiO/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst. This indicates a strong interaction between M (M = Pd, Co, Ir or Rh) and Ni via the electron transfer from M to Ni, resulting in an electron-deficient M and an electron-enriched Ni. This can be also verified by the shift of metal M binding energy. In the Pd 3d spectra of the recovered NiO-PdO/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, the binding energies at 335.5 eV and 340.8 eV are respectively ascribed to the Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  peaks of Pd<sup>0</sup> and the former increases 0.5 eV in comparison with the standard binding energy of 335.0 eV [14]. In the Co 2p spectra of the recovered NiO-Co<sub>3</sub>O<sub>4</sub>/ Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, the binding energy at 778.1 eV is assigned to the Co  $2p_{3/2}$  of Co<sup>0</sup>, which is shifted 0.2 eV towards a higher binding energy than the standard binding energy of 777.9 eV [9]. In the Ir 4f spectra of the recovered NiO-IrO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, the Ir  $4f_{7/2}$  peak of Ir<sup>0</sup> is located at 61.2 eV, shifting 0.3 eV to a higher binding energy compared to the standard binding energy of 60.9 eV [5]. In the Rh 3d spectra of the recovered NiO-Rh<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst, the Rh 3d<sub>5/2</sub> and Rh 3d<sub>3/2</sub> peaks of Rh<sup>0</sup> are located respectively at 307.8 eV and 312.5 eV and the former is shifted by 0.2 eV to a higher binding energy compared to the standard binding energy of 307.6 eV [15]. The above analyses confirm the existence of a strong interaction between Ni and M.

The above characterization results confirm the interaction between Ni and M. The interaction causes the decrease of NiO reduction temperature, being consistent with the results of the previous literatures [4–7]. What is more, NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (M = Pd, Co, Ir or Rh) catalysts show different reduction properties with respect to different M, thus to further affect the catalytic performance.



 $Pd^{2+} 3d_{3/2}$ 

recovered

348

fresh

recovered

fresh

recovered

72

fresh

810

2p<sub>1/2</sub>

sat.

 $\mathrm{Pd}^0 \mathrm{3d}_{\mathrm{3/2}}$ 

344

Co

800

 $^{+}4f_{7/2}$ 

68

 $Rh^{3+}_{...3d_{3/2}}$ 

MAMAAAAA

recovered

320

Fig. 4. XPS spectra of  $NiO-MO_x/Nb_2O_5$ -TiO<sub>2</sub> before and after reaction.

#### 4. Conclusions

The catalytic performance of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (M = Pd, Co, Ir or Rh) catalysts for direct synthesis of 2-PH from *n*-valeraldehyde were investigated and the results showed that adding MO<sub>x</sub> could promote reduction of NiO in the reaction process. NiO-Co<sub>3</sub>O<sub>4</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst showed the best catalytic performance; the selectivity of 2-PH reached 77.1% with a complete conversion of *n*-valeraldehyde. The characterization of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts were performed using H<sub>2</sub>-TPR, H<sub>2</sub>-TPD, XRD and XPS techniques and results indicated that an interaction between M and Ni and a hydrogen spillover from M site to Ni site played important roles in the reduction of NiO in reaction and in the promotion of catalytic performance of NiO-MO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.

# **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

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