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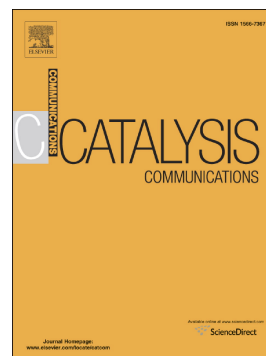
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Catalytic Performance of Ni/γ-Al$_2$O$_3$ for Hydrogenation of 2-Ethyl-2-hexenal

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Abstract: The effect of reaction conditions on the catalytic performance of Ni/γ-Al$_2$O$_3$ was investigated and the result showed that Ni/γ-Al$_2$O$_3$ showed excellent catalytic activity. However, the catalytic performance of the recovered Ni/γ-Al$_2$O$_3$ catalyst declined dramatically. The fresh and the recovered catalysts were comparatively analyzed by means of XRD, XPS and FT-IR techniques. The result demonstrated that the main reason for the activity decline of the recovered Ni/γ-Al$_2$O$_3$ catalyst is that the surface Ni has been reoxidized to NiO. After calcination and reduction, the recovered Ni/γ-Al$_2$O$_3$ catalyst could be reused four times without a significant decrease in its catalytic performance.

Keywords: 2-Ethyl-2-hexenal, 2-Ethylhexanol, Hydrogenation, Deactivation, Regeneration

1. Introduction

2-Ethylhexanol (2-EHO)，an important plasticizer alcohol，is mainly used in the production of plasticizers, coatings, adhesives and inks, etc. Nowadays, 2-EHO is produced via gas-phase hydrogenation of 2-ethyl-2-hexenal in the presence of ZnO-CuO catalyst [1], which is in high energy consumption. Therefore, development of economic and environmentally benign 2-ethyl-2-hexenal hydrogenation process and its catalyst is of academic and practical significance.

Mattos et al. [2] investigated the effect of Ni loading on the catalytic performance of Ni/γ-Al$_2$O$_3$ in liquid-phase hydrogenation of 2-ethyl-2-hexenal using a slurry reactor at atmospheric pressure. They found that Ni^{2+} species in the octahedral coordination was beneficial to the formation of 2-ethylhexanal and its selectivity was 100 % over the Ni/γ-Al$_2$O$_3$ with 7.3 (wt) % Ni. Yang et al. [3] studied the effect of Ni loading and reduction temperature of Ni/γ-Al$_2$O$_3$ on the hydrogenation of crude 2-ethylhexanol (the main byproducts were 2-ethylhexanal, 2-ethylhexenal and 2-ethylhexenol) in a fixed-bed reactor under the conditions of a reaction temperature of 120 ℃, a reaction pressure of 2.5 MPa and a liquid space velocity of 3.0 h^{-1}. The result indicated that the conversion of 2-ethylhexanal, 2-ethyl-2-hexenal and 2-ethylhexenol were separately 98.6 %, 99.99 % and 99.99 % using the Ni/γ-Al$_2$O$_3$ catalyst with Ni loading of 19.2 (wt) % prepared at the reduction temperature of 800 ℃. Deng et al. [4] studied the hydrogenation of 2-ethyl-2-hexenal catalyzed by Cu-Ni catalyst supported on silica gel and found that the mass fraction of 2-EHO could reach 99 % at the reaction temperatures of 90-125 ℃ and the pressures of 3-4 MPa.

It is obvious that the supported Ni-based catalysts, especially Ni/γ-Al$_2$O$_3$, shows excellent catalytic performance for the hydrogenation of 2-ethyl-2-hexenal. However, the reusability of catalyst especially the reason for deactivation and approach to regeneration has not been investigated in the above studies. In this paper, Ni/γ-Al$_2$O$_3$ was used to catalyze 2-ethyl-2-hexenal hydrogenation reaction. We aimed to clarify the reason for deactivation of Ni/γ-Al$_2$O$_3$ and the approach to its regeneration. Therefore, we investigated the effect of reaction conditions on the catalytic performance of Ni/γ-Al$_2$O$_3$ for hydrogenation of 2-ethyl-2-hexenal first and then the reusability of Ni/γ-Al$_2$O$_3$ catalyst.

2. Experimental

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The whole details of experimental part were depicted in the Supplementary information.

3. Results and discussion

3.1. Effect of reaction conditions on the catalytic performance of Ni/γ-Al$_2$O$_3$

3.1.1. Effect of catalyst amount

The effect of the amount of Ni/γ-Al$_2$O$_3$ with a Ni loading of 10 wt. % on 2-ethyl-2-hexenal hydrogenation reaction was investigated and the results are listed in Table S1. It can be seen that the conversion of 2-ethyl-2-hexenal was kept at 100 % while the yield of 2-EHO increased first and then decreased with the increase of Ni/γ-Al$_2$O$_3$ amount from 10 wt. % to 20 wt. %. When Ni/γ-Al$_2$O$_3$ amount was 10 wt. %, the yield of 2-EHO was lower (14.6 %) while the yield of 2-ethyhexanal was higher (76.8 %). The results suggest that the hydrogenation of C=C bond is easier than that of C=O bond. When Ni/γ-Al$_2$O$_3$ amount was 15 wt. %, the hydrogenation of C=O bond was promoted and the yield of 2-EHO was significantly increased to 93.8 %. When Ni/γ-Al$_2$O$_3$ amount was 20 wt. %, the yield of 2-EHO decreased slightly, possibly because excessive hydrogenation activity sites promoted side reactions. As a result, the formation of byproduct 2-ethylhexyl-2-ethylhexanoate caused the decrease in the yield of 2-EHO. Therefore, the suitable Ni/γ-Al$_2$O$_3$ amount was 15wt. %.

3.1.2. Effect of reaction temperature

The effect of reaction temperature on 2-ethyl-2-hexenal hydrogenation reaction was investigated. As can be seen from Table S2, the conversion of 2-ethyl-2-hexenal was also kept at 100 % while the yield of 2-EHO increased first and then decreased slightly at a reaction temperature ranging from 170 ℃ to 190 ℃. The yield of 2-ethyhexanal was higher but the yield of 2-EHO was lower at a reaction temperature of 170 ℃, suggesting that C=C bond hydrogenation requires lower temperature for its lower energy barrier. With the increase of reaction temperature,

the hydrogenation rate of C=O bond was significantly improved. 2-Ethylhexanal did not exist in the system and the yield of 2-EHO was 93.8 % at a reaction temperature of 180 ℃, indicating that C=O bond could be completely hydrogenated. However, the yield of 2-EHO decreased to 92.3 % with a continued increase of reaction temperature to 190 ℃, possibly due to the promotion of side reactions. In fact, 2-ethylhexylbutyrate, 2-ethylhexyl-2-ethylhexanoate and other byproducts increased by consuming some of 2-EHO, leading to the decrease in the yield of 2-EHO. Therefore, the suitable reaction temperature was 180 ℃. The experimental results also suggest that the hydrogenation of C=C bond is more preferential than that of C=O bond.

3.1.3. Effect of reaction pressure

The effect of reaction pressure on 2-ethyl-2-hexenal hydrogenation reaction was investigated. As can be seen from Table S3, 2-ethyl-2-hexenal was completely converted while the yield of 2-EHO increased first and then decreased with the increase of reaction pressure. The yield of 2-ethyhexanal was 80.1 % but the yield of 2-EHO was only 19.9 % at a reaction pressure of 1 MPa due to incomplete hydrogenation of the C=O bond. The hydrogenation rate of the C=C bond and the C=O bond was obviously improved at the reaction pressure of 2 MPa; 2-ethyl-2-hexenal was completely hydrogenated and the yield of 2-EHO reached the maximum of 93.8 %. The reaction pressure had no effect on the conversion of 2-ethyl-2-hexenal while the yield of 2-EHO decreased slightly with a continued increase of reaction pressure. That is probably because the larger reaction pressure aggravated the Tishchemko reaction of 2-ethyhexanal [5]. Therefore, the suitable reaction pressure was 2.0 MPa.

3.1.4. Effect of reaction time

The effect of reaction time on 2-ethyl-2-hexenal hydrogenation reaction was investigated and the

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results are shown in Table S4. The conversion of 2-ethyl-2-hexenal and the yield of 2-EHO increased while the yield of 2-ethyhexanal increased first and then decreased. There were a lot of 2-ethyhexanal and a small amount of 2-EHO in the product at the reaction time of 20 min, indicating that the main reaction was the C=C bond hydrogenation of 2-ethyl-2-hexenal. When the reaction time was prolonged to 40 min, 2-ethyl-2-hexenal was completely converted. Meanwhile, the yield of 2-ethylhexanal decreased and the yield of 2-EHO increased. With a continued increase of reaction time to 60 min, 2-ethylhexanal was completely converted into 2-EHO. When the reaction time was prolonged to 80 min, the yield of 2-EHO increased slowly and reached the maximum of 93.8 %. However, the yield of 2-EHO leveled off roughly with the increase of reaction time longer than 6 h. Therefore, the suitable reaction time was 80 min.

3.2. Reusability of Catalyst

The recovered Ni/γ-Al$_2$O$_3$ catalyst was treated in two ways. The first one was that the recovered Ni/γ-Al$_2$O$_3$ catalyst was washed with ethanol for three times and then dried at 110 ℃ for 8 h while the second one was that the recovered Ni/γ-Al$_2$O$_3$ catalyst was washed with ethanol for three times, dried at 110 ℃ for 8 h, calcinated at 500 ℃ for 4 h and reduced at 550 ℃ for 4 h. The catalytic performance of the recovered Ni/γ-Al$_2$O$_3$ catalyst separately treated in the two ways was evaluated and the results are listed in Table 1. It can be seen that the catalytic performance of the recovered catalyst treated by the first way declined significantly in the second run. However, the catalytic performance of the recovered catalyst treated by the second way did not decrease and the yield of 2-EHO remained unchanged even after reused for four times.

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Table 1 Reusability of Ni/γ-Al$_2$O$_3$

Catalyst	Run	X_{2E2H} / %	Y_{2EH} / %	Y_{2EHO} / %
Fresh	1	100	0	93.8
Recovered and treated by the first way	2	16.5	4.1	0
	2	100	0	93.7
Recovered and treated by the second way	3	100	0	94.2
	4	100	0	94.8
	5	100	0	93.9

Reaction conditions：T=180 ℃, P=2.0 MPa, t=80 min and a weight percentage of catalyst =15 %.

X_{2E2H}: conversion of 2-ethyl-2-hexenal; Y_{2EHO}: yield of 2-ethylhexanol; Y_{2EH}: yield of 2-ethylhexanal.

The fresh catalyst and the recovered Ni/γ-Al$_2$O$_3$ sample treated by the first way were analyzed by means of XRD and XPS techniques and the results are given in Figs. 1 and 2. As can be seen from Fig. 1, the intensity of characteristic diffraction peak of Ni in the recovered catalyst became weakened, possibly due to reoxidation of Ni to NiO. In order to analyze the change of diffraction peak of the fresh and recovered Ni/γ-Al$_2$O$_3$, XRD pattern of NiO/γ-Al$_2$O$_3$ was also given in Fig. 1. The peaks located at 2 theta = 37.25°, 43.24° and 62.88° were attributed to NiO [6]. However, the characteristic diffraction peaks of γ-Al$_2$O$_3$ and NiO were overlapped and could not be clearly distinguished. Through comparison of the diffraction peaks of a, b and c, we found that the characteristic diffraction peaks of the recovered Ni/γ-Al$_2$O$_3$ catalyst increased significantly but the characteristic diffraction peaks of Ni became weaker, suggesting that a part of Ni in the recovered Ni/γ-Al$_2$O$_3$ was reoxidized to NiO. In order to confirm the above speculation, XPS analyses of the fresh and recovered Ni/γ-Al$_2$O$_3$ were conducted and the result is showed in Fig. 2. According to the literatures [7-10], the binding energy of Ni2p3/2 in Ni^0 is 852.4±0.2 eV, the binding energy of Ni2p3/2 in Ni^{2+} is 856.7 eV and the binding energies of Ni2p1/2 in Ni^{2+} are 873 eV and 863 eV.

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As can be seen from Fig. 2, there was no Ni^0 but Ni^{2+} on the surface of the fresh and the recovered $Ni/\gamma-Al_2O_3$ catalysts, indicating that Ni on the surface of the fresh $Ni/\gamma-Al_2O_3$ was oxidized to NiO in the cooling stage of the reduction process and Ni in the recovered $Ni/\gamma-Al_2O_3$ was also reoxidized to NiO in the process of hydrogenation reaction.
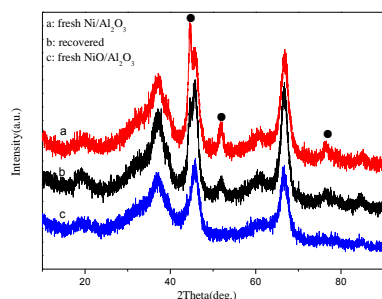

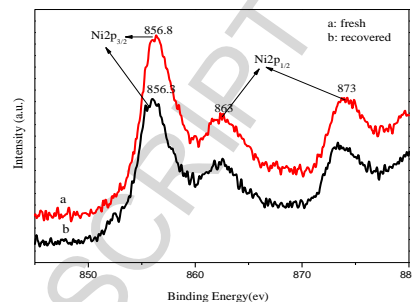Fig. 1. XRD patterns of the fresh and the recovered $Ni/\gamma-Al_2O_3$ catalysts

●：Ni

Fig. 2. XPS spectra of Ni 2p in the fresh and the recovered $Ni/\gamma-Al_2O_3$ catalysts

The fresh $Ni/\gamma-Al_2O_3$ catalyst was analyzed by TG-DTG technique and the result is illustrated in Fig. S1. The weight loss percentage was 3.0 % at 300 ℃, being attributed to the desorption of adsorbed water and volatile substances. The weight gain percentage was 0.6 % at 330 ℃ due to the oxidation of Ni to NiO. In addition, the mass change was not obvious at 530 ℃ and above, indicating that the catalyst was stable at a calcination temperature of 550 ℃. In this sense, the analysis result of H_2-TPR was not affected if the reduction temperature was higher than 550 ℃. Fig. 3 shows H_2-TPR curve of the calcined $NiO/\gamma-Al_2O_3$ catalyst while Fig. 4 shows H_2-TPR curves of the fresh catalyst and the recovered $Ni/\gamma-Al_2O_3$ catalyst treated by the first way. By comparing the H_2-TPR profile of the calcined catalyst ($NiO/\gamma-Al_2O_3$) with the fresh one ($Ni//\gamma-Al_2O_3$), it can be seen that the fresh $Ni/\gamma-Al_2O_3$ catalyst had obvious reduction peaks at 161.8 ℃ and 218.1 ℃ The two reduction peaks were attributed to the reduction of the dispersed NiO particles formed from the oxidation of Ni particles in the cooling stage in the reduction

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furnace. This kind of the dispersed NiO particles could be in situ reduced in the reaction process. For the recovered catalyst, however, there were not only the lower-temperature reduction peaks but also reduction peaks at 300~400℃ assigned to the reduction of NiO with large grains [11-13]. This kind of NiO was difficult to be in situ reduced.

Fig. 5 shows FT-IR spectra of the fresh and recovered Ni/γ-Al$_2$O$_3$ treated by the first way. There existed the infrared peaks of organic compounds in the recovered catalyst while there were no such infrared peaks in the fresh catalyst and the recovered catalyst after calcination. The weak and broad characteristic peaks at 3200~3700 cm^{-1} were assigned to water molecules or surface hydroxyl bond. The characteristic peak at 1630 cm^{-1} was assigned to hydroxyl group of water molecules. The absorption peak of alkyl group at 2800~2960 cm^{-1} in the recovered catalyst suggested that some kinds of organic compounds were adsorbed on the catalyst surface after reaction. The active sites were occupied by the adsorbed organic compounds and could not be effectively removed by ethanol washing and drying, thus lowering the catalytic performance.

In summary, the main reasons for the decrease in the catalytic performance of the recovered Ni/γ-Al$_2$O$_3$ catalyst treated by the first way are that the surface Ni has been reoxidized to NiO which cannot be in situ reduced and that the active sites are occupied by the adsorbed organic compounds. Therefore, the recovered catalyst needs to be calcinated and reduced in order to restore its catalytic performance.
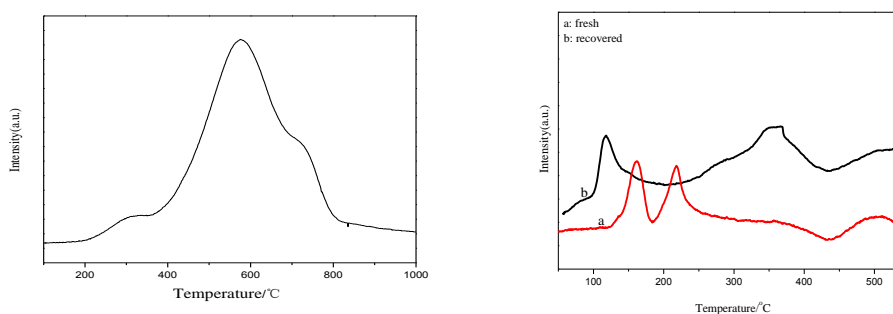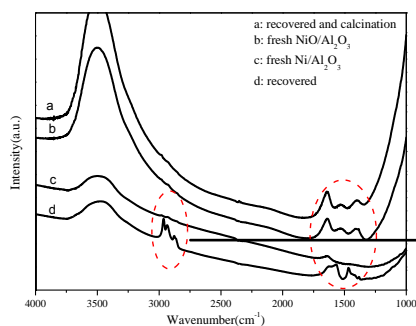

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Fig. 3. H$_2$-TPR curve of the calcined NiO/γ-Al$_2$O$_3$ catalyst

Fig. 4. H$_2$-TPR curves of the fresh and the recovered Ni/γ-Al$_2$O$_3$ catalysts

a: recovered and calcination
b: fresh NiO/Al$_2$O$_3$
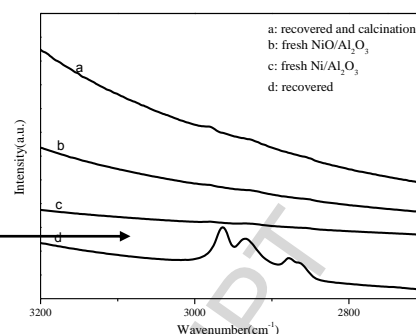c: fresh Ni/Al$_2$O$_3$
d: recovered

Fig. 5. FT-IR spectra of the fresh and the recovered Ni/γ-Al$_2$O$_3$ catalysts

4. Conclusion

The suitable reaction conditions for the hydrogenation of 2-ethyl-2-hexenal catalyzed by Ni/γ-Al$_2$O$_3$ were obtained as follows: a weight percent of Ni/γ-Al$_2$O$_3$ = 15 %, a reaction temperature of 180 ℃, a reaction pressure of 2.0 MPa and a reaction time of 80 min. Under the above reaction conditions, the conversion of 2-ethyl-2-hexenal and the yield of 2-EHO were 100 % and 93.8 %, respectively. The main reasons for the decline of hydrogenation activity of the recovered Ni/γ-Al$_2$O$_3$ catalyst are that the surface Ni has been oxidized to NiO and the active sites are occupied by some kinds of organic substances. The recovered Ni/γ-Al$_2$O$_3$ catalyst could be reused four times without a significant change in its catalytic performance after calcination and reduction.

Acknowledgments

Appendix A. Supplementary data

Materials and reagents; catalyst preparation; catalyst characterization; 2-ethyl-2-hexenal

hydrogenation reaction; product analysis; effect of reaction conditions on the catalytic

performance of Ni/γ-Al$_2$O$_3$; TG-DTG curves of the fresh Ni/γ-Al$_2$O$_3$ catalyst.

Supplementary data

Supplementary material

References

[1] J.Q. Ma, L. Xu, L. Xu, H. Wang, S. Xu, H. Li, S. Xie, H. Li, Highly dispersed Pd on Co−B amorphous alloy:

facile synthesis via galvanic replacement reaction and synergetic effect between Pd and Co, ACS Catal. 3

(2013) 985-992.

[2] A.R.J.M. Mattos, S.H. Probst, J.C. Afonso, M. Schmal, Hydrogenation of 2-ethyl-hexen-2-al on Ni/Al$_2$O$_3$

catalysts, J. Brazil. Chem. Soc. 15 (2004) 760-766.

[3] R.C. Yang, X.G. Li, J.S. Wu, X. Zhang, Z.H. Y.F. Zhang, J.T. Guo, Hydrotreating of crude 2-ethylhexanol over

Ni/Al$_2$O$_3$ catalysts: surface Ni species-catalytic activity correlation, Appl. Catal. A Gen. 368 (2009) 105-112.

[4] D. Deng, X. Zhang, Industrial appication domestic catalyst for liquid phase hydrogenation of 2-ethyl-hexanal,

Science & Technology in Chemical industry (Chinese) 10 (2002) 34-37.

[5] W.J. Xu, X.H. Liu, J.W. Ren, P. Zhang, Y. Wang, Y. Guo, Y. Guo, G. Lu, A novel mesoporous Pd/cobalt

aluminate bifunctional catalyst for aldol condensation and following hydrogenation, Catal. Commun. 11

(2010) 721-726.

[6] A. Fouskas, M. Kollia, A. Kambolis, Ch. Papadopoulou, H. Matralis, Boron-modified Ni/Al$_2$O$_3$ catalysts for

reduced carbon deposition during dry reforming of methane, Appl. Catal. A Gen. 474 (2014) 125-134.

[7] M.H. Amina, S. Putlaa, S.B.A. Hamid, S.K. Bhargave, Understanding the role of lanthanide promoters on the

structure–activity of nanosized Ni/γ-Al$_2$O$_3$ catalysts in carbon dioxide reforming of methane, Appl. Catal. A

Gen. 492 (2015) 160-168.

[8] F. Pompeo, D. Gazzoli, N. N. Nichio, Stability improvements of Ni/α-Al$_2$O$_3$ catalysts to obtain hydrogen from

methane reforming, Int. J. Hydrogen Energ. 34 (2009) 2260-2268.

[9] C. C. Torresa, J. B. Alderete, C. Mella, B. Pawelec, Maleic anhydride hydrogenation to succinic anhydride

overmesoporous Ni/TiO$_2$ catalysts: Effects of Ni loading and temperature, J. Mol. Catal. A Chem. 423 (2016) 441-448.

[10] D. Dissanayake, M. P. Rosynek, K. C. C. Kharas, J. H. Lunsford, Partial oxidation of methane to carbon monoxide and hydrogen over a Ni/AI$_2$O$_3$ catalyst, J. Catal. 132 (1991) 117-127.

[11] K.V.R. Chary, P.V.R. Rao, V.V. Rao, Catalytic functionalities of nickel supported on different polymorphs of alumina, Catal. Commun. 9 (2008) 886-893.

[12] P. Kim, H. Kim, J.B. Joo, W. Kim, I.K. Song, J. Yi, Effect of nickel precursor on the catalytic performance of Ni/Al$_2$O$_3$ catalysts in the hydrodechlorination of 1,1,2-trichloroethane, J. Mol. Catal. A Chem. 256 (2006) 178-183.

[13] N. Liang, X. Zhang, H. An, X. Zhao, Y. Wang, Direct synthesis of 2-ethylhexanol via n-butanal aldol condensation-hydrogenation reaction integration over a Ni/Ce-Al$_2$O$_3$ bifunctional catalyst, Green Chem. 17 (2015) 2959-2972.

The highlights of the manuscript can be described as follows:

- Ni/γ-Al$_2$O$_3$ shows excellent catalytic activity in hydrogenation of 2-ethyl-2-hexenal.

- The main reason for the activity decline of the recovered Ni/γ-Al$_2$O$_3$ is that Ni is oxidized to NiO.

- Ni/γ-Al$_2$O$_3$ has good stability after calcination and reduction of the recovered Ni/γ-Al$_2$O$_3$.