Effect of Lanthanides on the product distribution in the hydrogenation of aqueous levulinic acid over modified Ni/TiO_2 catalysts: Elucidation of reaction mechanism

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Abstract: In this study, we have developed an efficient route for the one step conversion of biomass derived aqueous levulinic acid to valeric acid (so called valeric bio-fuels) over modified Ni supported on titania catalysts in vapour phase at an ambient H_2 pressure. The formic acid adsorbed DRIFT spectra indicated an enhanced surface basicity upon modification of Ni/TiO_2 with La. It has been found that the La modified Ni/TiO_2 showed promising activity and stability in the formation of valeric acid. The fresh, reduced and some of the used catalysts were characterized by powder XRD, H_2-TPR, XPS, BET – surface area, pyridine and/or formic acid adsorbed DRIFT spectroscopy.

Keywords: Biomass, Valeric acid, DRIFTS.

1. Introduction

The hydrogenation of biomass (lignocellulose; inedible and inexpensive) derived levulinic acid (LA) to various γ-valerolactone (GVL) and valeric acid (VA) is an attractive process in bio-refinery [1]. The role of this transformation is pivotal, as it provides many alternative routes to the current existing fossil fuels which are unavoidable in the transportation sector [2]. Almost thorough investigation had been done on levulinic acid hydrogenation to GVL (a fuel additive, solvent, etc.) over both homogeneous and heterogeneous (noble and non-noble) catalysts in liquid phase as well as in vapour phase [3]. However, single step conversion of LA to VA (Fig. 1; a promising intermediate in the bio-fuel production) has been receiving attention in the valeric fuels due to the high energy density of VA [4]. Very few reports are appeared for the one-step production of VA from LA. In all of the reports, we see either use of noble metal or batch conditions at high H_2 pressures. There are very few reports on single-step conversion of LA to VA in the vapour phase at ambient H_2 pressure [4].

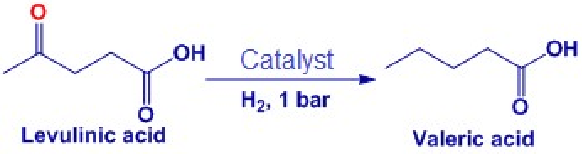

Fig. 1. Catalytic hydrogenation of aqueous levulinic acid.

Among several promoters; the La modified Ni/TiO_2, has demonstrated better activity towards valeric acid. A detailed study on La modified Ni/TiO_2 catalyst is carried out to optimize the product yield. The addition of La to Ni/TiO_2 drastically modified the reduction behavior of Ni species and surface acid - base properties which in turn influenced the hydrogenation activity to produce GVL along with valeric acid. The reduction behavior of La modified Ni/TiO_2 catalyst is investigated by H_2-TPR analysis. Nature of acid and basic sites on La modified Ni/TiO_2 catalyst is rationalized using pyridine and formic acid adsorbed DRIFTS and the Ni dispersion is estimated by N_2O titration. Long term stability tests and post characterization studies were also conducted on the optimized catalyst composition.

2. Experimental

All the catalysts were prepared using wet impregnation method. The experimental conditions for the preparation of the catalysts and techniques used for the characterization of the catalysts and activity testing of the catalysts are identical to the experimental conditions used in our earlier studies [4].

3. Results and discussion

The results obtained in the vapour phase conversion of LA to VA over the different promoters modified Ni/TiO_2 catalysts are presented in Table 1. Except Nd and Sm modified Ni/TiO_2 catalysts, no significant changes were observed in the LA conversion over all the catalysts, however major differences were observed in case of product distribution over these catalysts. The selectivity towards VA over the La modified Ni/TiO_2 catalyst is found to be high followed by Pr modified Ni/TiO_2. Except the La and Pr all the samples were found to be selective towards GVL rather than VA. At constant LA conversion the Pr modified Ni/TiO_2 showed lower VA selectivity than the Ni-La/TiO_2 catalyst. The selectivity towards GVL is more or less similar over all the catalysts except La and Pr modified samples. It appears that a surface acid-base site in conjunction with a metal (Ni^0) plays a crucial role on the product distribution. Particularly, the reduction of double bond in angelica lactone to GVL and its further transformation to valeric acid is most likely influenced by presence of acid-base sites on the catalyst surface. Hence a detailed investigation is carried out by the probe (pyridine and formic acid) adsorbed DRIFT spectroscopy to analyse the acid-base characteristics in conjunction with N_2O titration experiment for the estimation of Ni metal surface area.

Table 1. Conversion of levulinic acid over different catalysts. Reaction conditions: 275 °C, catalyst, 10wt% levulinic acid (in H_2O), H_2 flow: 20 mL min^{-1}.

Catalyst	LA conversion (%)	Selectivity (%) GVL	VA	Others[a]
Ni-La/TiO_2	9.5	35.5	39.8	24.7
Ni-Pr/TiO_2	8.0	49.3	22.3	28.4
Ni-Er/TiO_2	8.7	89.8	1.0	9.2
Ni-Nd/TiO_2	2.6	61.5	2.9	35.6
Ni-Sm/TiO_2	2.5	84.6	4.3	11.1
Ni-Y/TiO_2	7.2	80.2	5.9	13.9
Ni-Ce/TiO_2	6.1	79.4	5.7	14.9

[a] Others include, Angelica lactone (major), MTHF, pentanediol, etc.

4. Conclusions

La promoted Ni/TiO_2 is a promising catalyst for one step production of valeric acid (an important intermediate in the valeric fuels production) from biomass derived levulinic acid. Addition of La to Ni/TiO2 strongly influenced the further conversion of GVL to VA. The better VA selectivity was explained due to a synergy between Ni and La species The ring opening of GVL on La modified Ni/TiO_2 catalyst was rationalized by probe adsorbed DRIFT spectra and N_2O titration data.

References

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