

Catalyst-free TH of carbonyl compounds: comparison of H-donor activity of C₁-C₄ alcohols under sc-conditions

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Transfer hydrogenation (TH) demonstrates high potential in reduction of many organic^[1] and inorganic^[2] compounds. Therefore, TH is considered a real alternative to H₂ hydrogenation or metal hydrides which are widely used in organic chemistry. In the most cases, TH requires the catalysts^[3], however, examples of catalyst-free TH are also well-known^[4-6]. Catalyst-free TH occurs under more severe conditions^[4] but it does not involve heavy metals used as catalysts that is reasonable from ecological point of view. The transition of lower alcohols into supercritical (sc) state can provide specific properties including low surface tension and high dissolving power, which help to upgrade many polymeric materials, for example, graphene oxide^[7]. 2-PrOH is the most widely used alcohol as H-donor in TH^[8], nevertheless, MeOH and EtOH may be considered as H-donors in reduction for high molecular weight substrates. The main idea of this work is to compare H-donor activity of different primary and secondary alcohols. Menthone was used as H-acceptor because: 1) it contains only C=O bond which is able to join H-atoms and 2) formed menthols are stable under conditions used (350^oC, 120-210 atm).

Conversion of menthone under catalyst-free sc-conditions (350^oC, 120-210 atm) is similar for all 6 using alcohols and achieves 58-69% after 5 h (*Figure 1*, left). Selectivity of the process changes in the range 90-98% excluding methanol when the menthols yield is 73%. O-methylated menthols are found as byproducts that correlates with known activity of MeOH in alkylation. In TH catalyzed by Raney® nickel at 150^oC only secondary alcohols demonstrate activity: after 5 h of reaction the conversion of menthone achieves almost 100% for both 2-BuOH and 2-PrOH whereas no products were observed with all other alcohols (*Figure 1*, right).

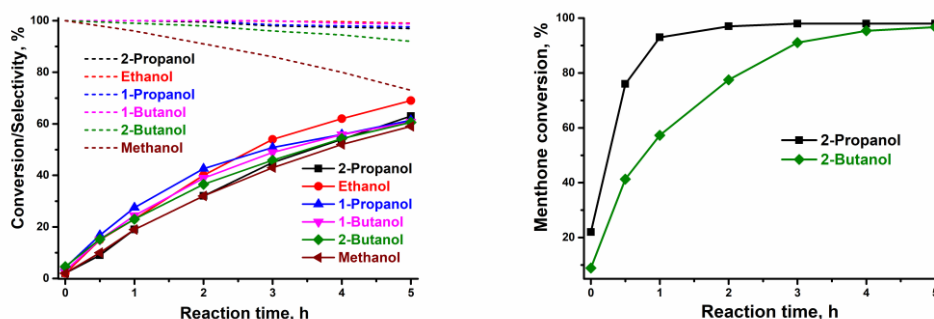


Figure 1. Conversion and selectivity of menthone in catalyst-free TH at 350^oC (left), and in catalyzed by Raney® nickel TH at 150^oC (right).

Additional experiment with 2-PrOH at 350^oC demonstrated that conversion of menthone is the same in both glass and metallic reactors, thus reactor walls do not play important role in TH under sc-alcohols.

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- [1] D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621–6686.
- [2] S. P. Gubin, E. Y. Buslaeva, *Russ. J. Phys. Chem. B* **2009**, *3*, 1172–1186.
- [3] A. A. Philippov, A. M. Chibiryayev, O. N. Martyanov, *Catal. Today* **2020**, *355*, 35–42.
- [4] A. Philippov, A. Chibiryayev, O. Martyanov, *J. Supercrit. Fluids* **2018**, *145*, 162–168.
- [5] A. M. Chibiryayev, I. V. Kozhevnikov, A. S. Shalygin, O. N. Martyanov, *Energy & Fuels* **2018**, *32*, 2117–2127.
- [6] A. M. Chibiryayev, I. V. Kozhevnikov, O. N. Martyanov, *Catal. Today* **2019**, *329*, 177–186.
- [7] M. Seo, D. Yoon, K. Seon, J. Won, J. Kim, *Carbon N. Y.* **2013**, *64*, 207–218.
- [8] T. Nakagawa, H. Ozaki, T. Kamitanaka, H. Takagi, T. Matsuda, T. Kitamura, T. Harada, *J. Supercrit. Fluids* **2003**, *27*, 255–261.