ISGC 2019
May 13rd - 17th

N°363 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Biomass conversion

Niobium oxide prepared through a novel supercritical CO2-assisted method as versatile heterogeneous catalyst for the synthesis of 5-HMF and azoxybenzene

AUTHORS

Yehan TAO / PRODUCT TECHNOLOGY GROUP, ENTEG, UNIVERSITY OF GRONINGEN., NIJENBORGH 4, GRONINGEN
Francesco PICCHIONI / PRODUCT TECHNOLOGY GROUP, ENTEG, UNIVERSITY OF GRONINGEN., NIJENBORGH 4, GRONINGEN
Paolo PESCARMONA / PRODUCT TECHNOLOGY GROUP, ENTEG, UNIVERSITY OF GRONINGEN., NIJENBORGH 4, GRONINGEN

PURPOSE OF THE ABSTRACT

1. Background and motivation

Nb2O5 possesses both Brønsted and Lewis acid sites, whose quantity and strength can be tuned depending on the oxide structure. Exploiting this feature, Nb2O5 found broad applications in acid-catalyzed reactions. Here we present a new strategy to tune the acid sites of Nb2O5 by preparing the material (Nb2O5-scCO2) using a novel supercritical CO2 (scCO2)-assisted precipitation method. The physical properties of scCO2 as reaction medium differ from those of traditional organic solvents because the dissolving power and density can be tuned by simply adjusting the pressure or temperature. ScCO2 is favorable for synthesizing uniform nanomaterials owing to its ?zero? surface tension, high diffusivity in supercritical condition, ease of separation from reactants and products, and low toxicity. Additionally, CO2 has widespread availability. The prepared Nb2O5-scCO2 was tested as heterogeneous catalyst for two relevant reactions in the context of green chemistry: (1) the one-pot conversion of glucose (i.e. most abundant lignocellulosic monosaccharide) into 5-(hydroxymethyl) furfural (5-HMF) and (2) the oxidative coupling of aniline into azoxybenzene with H2O2 as environmental friendly oxidant.

2. Result and discussion

Reaction 1: Glucose conversion to produce 5-(hydroxymethyl)furfural

The direct conversion of glucose sparked considerable scientific and industrial interest because it provides a straightforward access to 5-HMF, which is an attractive feedstock chemical for both furan and nonfuranic derivatives (see figure 1). One-pot 5-HMF formation from glucose proceeds by isomerization of glucose to fructose (catalyzed mainly by Lewis acid), followed by dehydration of fructose (catalyzed mainly by Brønsted acid). The catalyst should be able to selectively convert glucose into 5-HMF with a low weight ratio between catalyst and substrate (RC/S, e.g. ?1), and maximally limit 5-HMF polymerization to humins or re-hydration to form formic acid and levulinic acid, which can be realized by performing the reaction at a relatively low temperature (e.g. 120 ?C). By using a biphasic water/methyl isobutyl ketone (MIBK) as the reaction medium, 77% of glucose conversion and 46% of 5-HMF selectivity was obtained over Nb2O5-scCO2 catalyst at 120 ?C after reaction time of 3 h with an RC/S of 1 (lower compared to literature).

Reaction 2: Aniline oxidative coupling to produce azoxybenzene

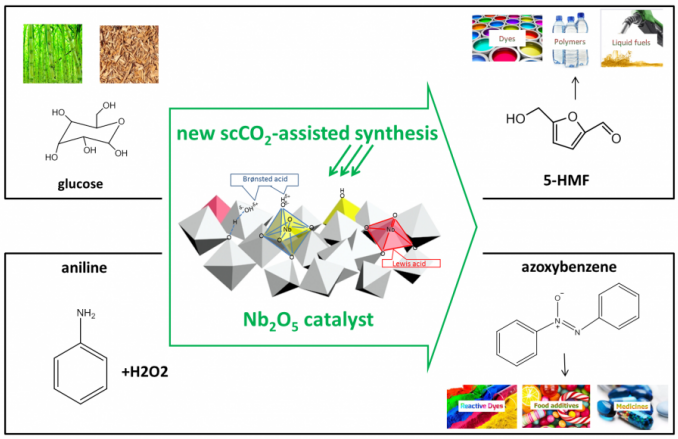
Azoxy derivatives are high-value chemicals widely used in industry such as dyes, reducing agent and therapeutic medicines (see figure 1). They can be obtained by catalytic oxidation of anilines in the presence of an oxidant. The catalyst should be able to control the selectivity to the target azoxybenzene in the midst of all possible oxidation product (e.g. nitrosobenzene, nitrobenzene, azobenzene). Here we report for the first time that Nb2O5 can be utilized as catalyst in this reaction to produce azoxy products. An aniline conversion of 87% (stoichiometric

maximum 93% with the employed H_2O_2 ratio of 1.4) with azoxybenzene selectivity of 94% was achieved in 45 min over Nb_2O_5-$scCO_2$ with a very low RC/S (10 mg catalyst vs. 1.86 g aniline) without external heating (the reaction is exothermic).

3. Conclusion

The utilization of $scCO_2$ as reaction medium allowed preparing a highly active Nb_2O_5 heterogeneous catalyst. Nb_2O_5-$scCO_2$ efficiently catalyzed the one-pot glucose conversion to 5-HMF and the aniline oxidative coupling to azoxybenzene, achieving higher selectivity than a counterpart catalyst prepared without $scCO_2$. Moreover, the Nb_2O_5-$scCO_2$ catalyst shows excellent reusability.

FIGURES



Reaction	Reaction condition	Conversion	Product selectivity
One-pot glucose conversion	10mg/ml glucose, 4ml MIBK/H_2O, 3h,120° C, 40mg Nb_2O_5-$scCO_2$ as catalyst	77%	5-HMF 46% + fructose 3% + mannose 3% + formic acid <1%
Aniline oxidative coupling	20mmol aniline, 30mmol H_2O_2 (30wt%) 10ml ethanol, start from RT, 10mg Nb_2O_5-$scCO_2$ as catalyst	88%	azoxybenzene 94% + nitrosobenzene 6%

FIGURE 1
Figure 1
Reactions catalyzed by Nb2O5-scCO2

FIGURE 2
Figure 2
Catalytic performance over Nb2O5-scCO2

KEYWORDS
niobium oxide catalyst | supercritial co2 synthesis | glucose conversion | aniline oxidative coupling

BIBLIOGRAPHY

[1] K. Nakajima, Y. Baba, et al. JACS, 2011, 133 (12), 4224-4227.
[2] HT. Kreissl, K. Nakagawa, et al. J. Catal. 2016, 338, 329-339.
[3] S. Ghosh, SS. Acharyya, et al. Green Chem. 2015, 17, 1867.