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Kinetics of the solvent-free hydrogenation of 2-methyl-3-butyn-2-ol over a structured Pd-based catalyst

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ABSTRACT

The solvent-free selective hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) was studied over a Pd/ZnO structured catalyst and compared to its behavior in water-assisted conditions. The catalytic behavior was correlated with the surface properties of the catalysts which were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. The catalyst showed high selectivity and stability with the performance being superior to that of the industrial Lindlar catalyst (50%). The addition of a sulphur-containing modifier in the reaction mixture was found to affect the activity and to hinder the over-hydrogenation reaction. The MBE yield of ~97% was attained at MBY conversion >99%. The reuse of the catalyst showed that it deactivated by a 38% and that its selectivity slightly increased (~0.5%) over 10 runs. The reaction kinetics was modeled using a Langmuir–Hinshelwood mechanism considering competitive adsorption for the organic species and dissociative adsorption for hydrogen. The kinetic experiments were planned and the results analyzed following a design of experiments (DOE) methodology. This approach led not only to a robust model that predicts the reaction rate in a wide range of reaction conditions but also to the determination of its kinetic parameters.

1. Introduction

The selective catalytic hydrogenation of alkynols to alkenols is an important process in the fine chemicals industry [1,2]. Pd-based catalysts are known to give the highest selectivity and yield [3]. Their performance is strongly influenced by the dispersion of the active metal [4,5], the nature of the support [6,7] and the use of promoters [8] and additives [9].

In industry, these reactions are mostly carried out in slurry reactors with Lindlar catalyst [10]. In such cases, the influence of mass transfer may decrease the catalyst performance [11] and thus must be taken into consideration. Furthermore, the Lindlar catalyst used as a fine powder is difficult to handle requiring filtration after the reaction.

To overcome these problems, a continuous staged bubble column reactor (SBCR) has been suggested [12]. It presents improved mass transfer between the liquid and the gas phase while hindering backmixing [13,14]. The operation of SBCR requires an effective structured catalyst to be used as catalytic stages.

Recently, a structured Pd-based catalyst supported on sintered metal fibers (SMF) has been developed in our group [15]. The SMF are coated with a ZnO layer on which pre-synthesized Pd nanoparticles are deposited. The catalyst showed an excellent performance in the water-assisted selective hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) with a complete hindrance of the over-hydrogenation reaction to 2-methyl-3-butan-2-ol (MBA). This high selectivity towards MBE was due to the formation of an inter-metallic phase (PdZn) obtained after subjecting the catalyst to a high-temperature treatment under hydrogen [15]. Furthermore, the SMF panels coated with ZnO presented an open structure and, thus, were found to have a low-pressure drop in an SBCR [13].

In this work, the kinetic behaviour of a Pd/ZnO/SMF structured catalyst in the solvent-free selective hydrogenation of MBY to MBE was studied in order to evaluate its feasibility for the application in an SBCR. MBE is an intermediate in the synthesis of vitamins A and E and perfumes (Fig. 1). The catalyst was characterized by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD) and X-ray

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Abbreviations: AAS, atomic absorption spectroscopy; ANOVA, analysis of the variance; BE, binding energy; BPC, Büchi pressflow controller; CCD, central composite design; D, dimers; DF, degrees of freedom (ANOVA); DOE, design of experiments; *F*, *F*-ratio (ANOVA); MBA, 2-methyl-3-butan-2-ol; MBE, 2-methyl-3-buten-2-ol; MBY, 2-methyl-3-butyn-2-ol; MS, mean square (ANOVA); OFAT, one-factor-at-a-time; *P*, probability of being noise (ANOVA); SBCR, staged bubble column reactor; SMF, sintered metal filters; SS, sum of squares (ANOVA); XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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Nomenclature

a_0	constant effect of the CCD design
a_i	main half effects of the CCD design
a_{ii}	second-order half effects of the CCD design
a_{ij}	first-order interaction half effects of the CCD design
A	apparent pre-exponential factor ($m^3\ mol_{Pd}^{-1}\ s^{-1}$)
C_{H_2}	hydrogen bulk concentration ($mol\ m^{-3}$)
C_i	concentration of i ($mol\ L^{-1}$)
E_a	apparent activation energy ($kJ\ mol^{-1}$)
k_i'	apparent kinetic constant of the reaction i ($L\ mol_{Pd}^{-1}\ s^{-1}$)
K_i	adsorption constant of i ($L\ mol^{-1}$)
K_i^*	adsorption constant of the intermediate i
M_i	molecular weight of i ($g\ mol^{-1}$)
n_{Pd}	amount of active material in the catalyst (mol)
r_i	rate of the reaction i ($mol\ mol_{Pd}^{-1}\ s^{-1}$)
r_i^0	initial reaction rate ($mol\ mol_{Pd}^{-1}\ s^{-1}$)
S	selectivity towards MBE (%)
u_i	standardized variable of the CCD design
V_L	volume of liquid in the reaction (L)
w_i	mass fraction (%)
x_i	molar fraction (%)
X	conversion of MBY (%)

Greek letter

ρ_0	density of the reaction mixture ($g\ L^{-1}$)

photoelectron spectroscopy (XPS). Its performance was compared to that of the industrial Lindlar catalyst. The catalyst reuse and the influence of a sulphur-containing additive were also studied. The reaction kinetics was modelled based on a Langmuir–Hinshelwood mechanism considering competitive adsorption for the organic species and dissociative adsorption of hydrogen [16]. The planning and analysis of the kinetic experiments was done through a design of experiments (DOE) methodology. In this kind of approach, the parameters that affect a given response are varied simultaneously. Classically, the estimation of the apparent coefficients is done by performing one-factor-at-a-time (OFAT) experiments, which vary only one parameter while keeping the others fixed. However, statistically designed experiments, or DOE, vary several factors simultaneously [17]. In general, DOE presents many advantages as compared to OFAT approaches being less time consuming for the same amount of information obtained.

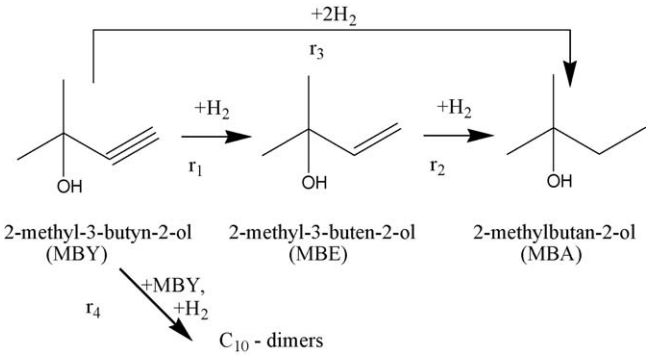

Fig. 1. Reaction scheme for the hydrogenation of MBY.

Moreover, the values of the model parameters are more accurate and the interaction between factors can be estimated systematically. DOE also provides information for a larger experimental region using the same amount of experimental data [17]. The most important feature of DOE is that the results obtained are backed by a solid statistical background [18]. The application of DOE to obtain kinetic data is not recent although it has not been hitherto widely used [19–21].

2. Experimental

2.1. Materials

SMF made of FeCrAl alloy fibers (Cr 20%, Al 4.75%, Y 0.27%, other elements ~1–2%, Fe balance) in the form of a uniform porous panel (0.29 mm thickness, 71% porosity, 20 μm fiber thickness, 675 g/m^2) [22] were used as a structured support.

2-Methyl-3-butyn-2-ol (purum, ≥99%), 2-methyl-3-buten-2-ol (purum, ≥97%), 2-methyl-2-butanol (purum, ≥98%) and ZnO powder were purchased from Fluka and used as received. Hydrogen (≥99.99% purity) was acquired from Carbagas, Switzerland. Bidistilled water was used throughout this work.

2.2. Catalyst preparation

The preparation of the structured Pd/ZnO/SMF catalyst used throughout this work was described in detail elsewhere [15]. Briefly, the SMF panels were degreased, calcined and covered with a thin film of ZnO via a sol–gel method, which was found to be inert in the studied reaction. Pd nanoparticles prepared beforehand via electrostatical stabilization were deposited on ZnO/SMF material. The only difference in the procedure consists in the suppression of the last reduction step at high temperature. As a consequence, there was no deliberate formation of the intermetallic PdZn phase.

The powdered 5 wt.% Pd/ZnO catalyst was prepared by wet impregnation using the same Pd-nanoparticle solution of an adequate concentration. The ZnO powder was previously calcined to eliminate all residues at 693 K for 3 h.

2.3. Catalyst characterization

To determine the amount of Pd, the catalyst was dissolved in hot nitric acid and the sample was analyzed by atomic absorption spectroscopy (AAS) via a Shimadzu AA-6650 spectrometer with an air-acetylene flame.

An ultrasonic adherence test for the mechanical stability of the catalyst was carried out using an ultrasonic bath (Bransonic ultrasonic cleaner, Branson Ultrasonic Corp., USA). The catalyst was immersed in isopropanol and sonicated for 10 min.

XRD analyses were carried out in a Siemens D 500 diffractometer using Cu Kα radiation. The spectra of the 5% Pd/ZnO powder samples were recorded in a rapid scanning mode (4.0 s/step, 2θ step size of 0.04°) in a 2θ range of 30–50°. For the calculation of the particle size of Pd, Scherrer's equation was used.

XPS of the powder 5% Pd/ZnO samples was performed using an Axis Ultra ESCA system (Kratos, Manchester) with monochromated Al Kα radiation (1486.6 eV) and an X-ray power of 150 W. The binding energy (BE) values were referenced against a C 1s = 285.0 eV line.

2.4. Hydrogenation experiments

The reactions were carried out in a semi-batch stainless steel reactor (250 mL autoclave, Büchi AG, Uster, Switzerland) equipped