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Preparation and Characterization of a Solid Acid Catalyst from Commercial Niobia Hydrate

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A commercially available niobia hydrate, which is an industrial intermediate in the production of pure niobia, was prepared, characterized, and tested as a solid acid catalyst. The gas phase esterification of acetic acid with ethanol was used as a simple model reaction for the determination of the acidity and the catalytic activity. The kinetic evaluation of the experiments includes an estimation of mass transport limitation as well as a mechanistic study.

1 Introduction

The use of solid acids instead of liquid mineral acids for catalytic applications is characterized by higher process stability and being environmentally less harmful, as well as

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being less dangerous processes. Niobic acid, a water-containing niobia, has proved to be a suitable catalyst for several reactions [1–4]. Especially for acid catalyzed reactions with water as a reactant or reaction product, niobic acid keeps a high activity, whereas other solid acids partly lose their activity in contact with water or steam. Thus, niobic acid can be used as a catalyst in several reactions [4]. In our experimental studies we could observe catalytic activity for the following reactions: oxidative dehydrogenation of propane, esterification of acetic acid with ethanol and 2-propanol, *N*-alkylation of aniline with ethanol, and dehydration of 2-propanol. The esterification was chosen as a model reaction for the characterization of the catalyst, since side reactions, etherification and dehydration of ethanol, were shown to appear only at high temperatures and can be neglected in the chosen temperature range of 150–220 °C [5]. This is a great simplification for conversion measurement and development of kinetic models.

Our previous research focused on the *N*-alkylation of aniline with ethanol [6, 7] over an industrial niobic acid catalyst. By means of a kinetic study we could show that the reaction pathway occurs via an adsorbed ethoxy species. The observed kinetics agreed well with the Eley/Rideal mechanism. From these results we suggested adsorbed ethanol as the transition state to be attacked by aniline out of the gas phase. One aim of this study was to investigate similarities between *N*-alkylation and esterification concerning the ethoxy group as the transition state. Several studies on the heterogeneously catalyzed esterification of acetic acid with ethanol revealed inconsistent theories concerning the microkinetics. Besides the mainly postulated Langmuir/Hinshelwood mechanism (LH) [8–11], Eley-Rideal kinetics with ethanol as the adsorbed species was also found in the literature [8–12]. A change in the mechanism from LH to ER (dual-site to single site) depending on the chain length of the alcohols (short to long chain) was also proposed [13]. Since alcohols adsorb more strongly on the catalyst surface, this theory was explained by sterical hindrance of the adsorption of carboxylic acid by the long alkyl chains of the alcohol. A second explanation could also be a greater influence of the catalyst itself on the reaction pathway, since the studies were carried out over ion-exchange resins, zeolites, or other solid acids.

Another question for our experimental program was the suitability of a commercial niobia hydrate as a catalyst precursor. The influence of the pelletizing pressure, as well as particle size and the modification of the catalytic activity by treatment with phosphoric and sulfuric acid were tested.

2 Experimental

The catalytic measurements were carried out in a stainless steel tubular reactor (l = 130 mm, d = 10 mm), which was heated by a surrounding aluminum block with six cartridge heaters (each 120 W). The pelletized catalyst, usually 1.0 g,

was fixed between two layers of pyrex beads. Inside the reactor, a thermocouple tube was installed, which allowed the measurement of the axial temperature profile in the catalyst bed. The liquid reactants, ethanol and acetic acid, were mixed in a given ratio and pumped into the reactor by a HPLC-pump. Evaporation and heating of the reactants occurred in the pyrex bead layer upon the catalyst bed. The conversion of the reaction was determined with a gas chromatograph (Intersmat IGC 120 ML, column: 50 m × 0.53 mm CP-Wax, carrier gas: He) via water formation.

3 Results and Discussion

3.1 Characterization and Stability of the Niobia Hydrate

Niobia hydrate was provided by the H. C. Starck company as white powder in a particle size fraction of $< 50\ \mu$m. The loss on ignition of 36.4 wt % after 2 h at 2000 °C is mainly composed of water and ammonia, both residues of the precipitation process, which could be detected with IR-spectrometry. As expected, the material is amorphous and no crystalline niobia Nb_2O_5 could be detected by XRD. For catalytic testing, 2 g of the powder was compressed in a stainless steel stamp (d = 26 mm) for 5 min at 200 bar. The pellets were crushed and a particle size fraction of 710–850 μm was obtained by sieving. Before preparation of a catalyst sample, the particles were dried for 2 h at 150 °C in air, to ensure a unified water content and thereby a uniform amount of niobia in the tested catalyst. The stability of the catalyst under reaction conditions was determined before kinetic experiments by a series of screening experiments. By varying the reaction conditions, the conversion[1] X was adjusted in the medium range, where changes in the activity are detected with high sensitivity. The catalyst shows no aging or deactivation with time on stream for up to one week, as expected [5].

3.2 Influence of the Pelletizing Pressure and Particle Size on the Activity

In order to enable kinetic modeling, mass transport limitations were excluded. Different particle size fractions, which were also pelletized with different pressures, were tested for their catalytic activity (see Fig. 1). For the particle size fractions at a constant plateau of activity, the absence of mass transport limitations was assumed.

It can clearly be seen that neither the pelletizing pressure nor particle diameter have a significant influence on the reaction rate in the investigated range. The deviation at the smallest and largest particle size fractions, respectively, compressed at 150 bar, as well as the slight scattering of the mea-

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1) List of symbols at the end of the paper.
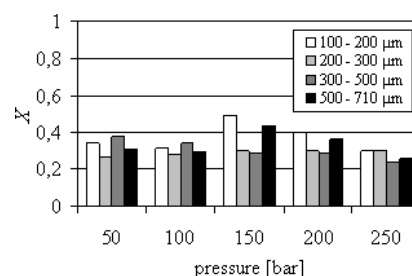
Figure 1. Dependency of conversion on pelletizing pressure (50–250 bar) and particle diameter (100–710 μm); m_{Kat} = 1.0 g, T = 150 °C, $\dot{V}_l$ = 0.05 mL/min, n_{EtOH}:n_{AcOH} = 1.

sured values of ± 5 %, may be referred to the use of a multi channel tube pump for dosing the reactant mixture in the screening aperture. The 100–200 μm fraction was also used for BET measurements (Micromeritics 2375, Adsorbents: N_2, T = 77 K). The obtained data are assembled in Tab. 1.

Table 1. BET surface area and pore diameter of niobia hydrate as functions of pelletizing pressure of the catalyst particles, d = 100–200 μm.

| Pressure [bar]	BET surface area [$m^2 g^{-1}$]	Pore diameter [nm]
50	121.6	3.54
100	115.6	4.00
150	107.5	3.71
200	98.3	4.09
250	92.3	3.94

Instead of the pore diameter, which seems to be independent of the pelletizing pressure at about 4 nm, the BET surface area decreases with increasing pressure. Since this does not reflect on the catalytic activity, the particles were proved to be gradient-free, which is a necessary condition for microkinetic modeling.

3.3 Further Modifications and Comparison of Activity

It is well known that the activity of solid acid catalysts can be influenced by treatment with phosphoric or sulfuric acid. In order to add phosphate and sulfate groups to the surface, the niobia hydrate was kept for 15 h in acidic solutions with different concentrations at ambient temperature. After this exposure time, the samples were filtered, washed with deionized water until a neutral pH was reached, and then dried overnight at 80 °C. For catalytic measurements the obtained powder was pelletized as described in Section 3.1. The activity of these samples in the esterification of acetic acid with ethanol is shown in Fig. 2.

The activity could not be enhanced with the mineral acid treatment; contrary to expectations, the conversion in the investigated esterification decreased with increasing concentration of both acids. Since the activity of niobic acid catalysts can indeed be increased with this method for other reactions [4], the esterification may be catalyzed at different
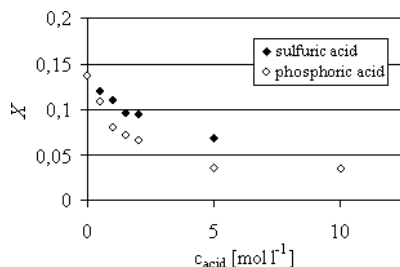
Figure 2. Influence of phosphoric and sulfuric acid treatment on the catalytic activity of niobia hydrate in the esterification of acetic acid with ethanol; m_{Kat} = 0.5 g, T = 150 °C, $\dot{V}_l$ = 0.05 mL/min, n_{EtOH}:n_{AcOH} = 1.

active centers than, e.g., the alkylation of benzene. Possibly a dehydration of the niobia hydrate occurs due to the strong hygroscopic acids. Consequently, one would conclude that the esterification is catalyzed by Brönstedt-acidic centers, while the alkylation is predominantly catalyzed by Lewis-acidic centers. A detailed analysis of these correlations was not included in this study.

A further attempt to increase the activity by combination with another material was the grinding of the niobia hydrate with alumina. The equimolar mixture of the substances was milled under water, and the resulting powder was dried and treated as described in section 3.1. The comparison with the pure substances is shown in Fig. 3. Alumina alone provides a very low activity; nevertheless, the conversion with the mixture is only a little smaller than that of pure niobia hydrate. This method of catalyst "dilution" seems to be neither a suitable method of increasing activity due to a better accessibility of the active sites, nor a way of inducing an interaction between both materials resulting in better catalytic performance.

A comparison of activity among several niobic acid catalysts is also given in Fig. 3. Data for an industrial catalyst (Bayer) and niobic acid produced by CBMM (Companhia Brasileira de Metalurgia e Mineração) were available. Both catalysts provided a higher activity in the esterification reaction. The value for the CBMM catalyst is interpolated from literature data and given with the corresponding error bar. The niobic acid from Bayer was clearly shown to lose activity when treated with the same pelletizing procedure as the
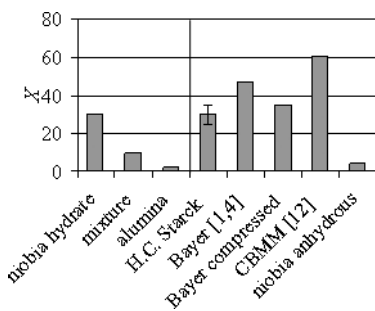

Figure 3. Comparison of activity among different niobic acid catalysts and niobia, as well as via grinding with alumina modified niobia in the gas phase esterification of acetic acid with ethanol; m_{Kat} = 1.0 g, T = 150 °C, $\dot{V}_l$ = 0.05 mL/min, n_{EtOH}:n_{AcOH} = 1.

H. C. Starck niobia hydrate. This indicates a possibility for improvement of the catalyst preparation method, which could not be fully investigated in our experimental study. For a further comparison, the activity of dry niobia Nb_2O_5 was determined, which was very low, as expected. An attempt to activate this ceramic substance with steam in an autoclave failed.

3.4 Kinetic Modeling of the Esterification

For kinetic modeling the differential method was applied. The measurement of the initial reaction rates with different feed compositions aimed to differentiate between the Eley/Rideal and Langmuir/Hinshelwood mechanisms. The thermodynamic equilibrium in the gas phase (see Fig. 4) allows this procedure, a conversion of 5–10 % was adjusted by the flow rate. A homogeneous gas phase contribution to the reaction can be neglected up to a temperature of 450 °C [12].
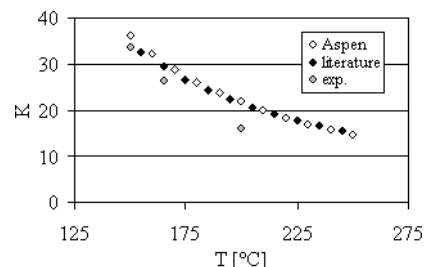

Figure 4. Equilibrium constant of the esterification of acetic acid with ethanol in the gas phase as a function of temperature; calculated with Aspen and literature data [14] and experimental values [15].

For model differentiation four possible mechanisms were taken into consideration. ER1 describes the adsorption of ethanol, ER2 the adsorption of acetic acid, while the corresponding component reacts directly from the gas phase (Eley/Rideal mechanism). The Langmuir/Hinshelwood mechanism differs with regard to the adsorption sites. LH1 describes the reaction with competitive adsorption of ethanol and acetic acid, while LH2 takes into consideration that the two reactants may prefer to adsorb on different active sites. The reaction products were assigned to the different adsorption sites by evaluation of isotope studies [8], but still needed experimental confirmation, e.g., by detailed kinetic studies. In order to calculate the partial pressures, one had to consider the dimerization of acetic acid in the gas phase. In our model we assumed that both species, i.e., the monomer and dimer (after dissociation and leaving one monomer in the gas phase), are able to adsorb and react. The subsequent equations, corresponding to the discussed models, were used for data evaluation (see Tab. 2).

The experimentally determined reaction rates as functions of the feed composition are shown in Fig. 5. The four rate laws were fitted to these data using the least squares method. It can clearly be seen that only model LH2 is able to de-

Table 2. Considered reaction rate laws for the model differentiation.

	Reaction rate		Initial reaction rate $(p_{H_2O}, p_{AcOEt} = 0)$	
LH1	$r = \dfrac{kK_1K_2\left(p_{EtOH}p_{(AcOH)_2} - \frac{p_{H_2O}p_{AcOEt}}{K}\right)}{\left(1 + K_1p_{EtOH} + K_2p_{(AcOH)_2} + K_3p_{H_2O} + K_4p_{AcOEt}\right)^2}$	(1)	$r_0 = \dfrac{kK_1K_2p_{EtOH}p_{(AcOH)_2}}{\left(1 + K_1p_{EtOH} + K_2p_{(AcOH)_2}\right)^2}$	(2)
LH2	$r = \dfrac{kK_1K_2\left(p_{EtOH}p_{(AcOH)_2} - \frac{p_{H_2O}p_{AcOEt}}{K}\right)}{(1 + K_1p_{EtOH} + K_4p_{AcOEt}) \cdot \left(1 + K_2p_{(AcOH)_2} + K_3p_{H_2O}\right)}$	(3)	$r_0 = \dfrac{kK_1K_2p_{EtOH}p_{(AcOH)_2}}{(1 + K_1p_{EtOH})\left(1 + K_2p_{(AcOH)_2}\right)}$	(4)
ER1	$r = \dfrac{kK_1\left(p_{EtOH}p_{(AcOH)_2} - \frac{p_{H_2O}p_{AcOEt}}{K}\right)}{1 + K_1p_{EtOH} + K_3p_{H_2O}}$	(5)	$r_0 = \dfrac{kK_1p_{EtOH}p_{(AcOH)_2}}{1 + K_1p_{EtOH}}$	(6)
ER2	$r = \dfrac{kK_1\left(p_{EtOH}p_{(AcOH)_2} - \frac{p_{H_2O}p_{AcOEt}}{K}\right)}{1 + K_1p_{(AcOH)_2} + K_3p_{H_2O}}$	(7)	$r_0 = \dfrac{kK_1p_{EtOH}p_{(AcOH)_2}}{1 + K_1p_{(AcOH)_2}}$	(8)
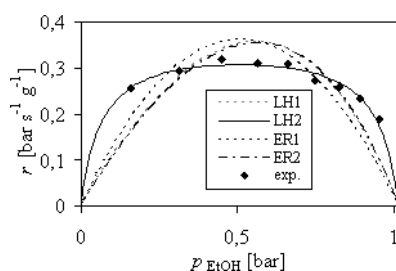
Figure 5. Reaction rate of the esterification of acetic acid with ethanol as a function of the molar ratio of reactants in the feed. Fit of the experimental data with the four described microkinetic models LH1, LH2, ER1 and ER2; $m_{Kat} = 1.0$ g, $T = 150\,°C$. Fitting results for LH2: $k = 4.9$ bar/s; $K_1 = 14.7$ bar^{-1}; $K_2 = 12.3$ bar^{-1}.

scribe our experimental results sufficiently. This is confirmed by the quality of fit (see Tab. 3).

The plateau-shape of the reaction rate in the range of equal partial pressures may theoretically also be referred to as an influence of product desorption on the reaction rate. In cases of similar desorption and surface reaction rates, a similar curve shape can be expected. Such an influence rarely appears, and is unlikely in this case due to the weak interaction of the reaction products with the catalyst surface. All the kinetic studies found in the literature confirm the assumption of the surface reaction as the rate determining step of the esterification.

By varying the temperature in the range 150–220 °C, an "effective activation energy" of the reaction was determined to be $E_{A,eff} = 70.7$ kJ mol^{-1}. No literature data were found for comparison. The activation energy was obtained from the reaction rate rather than from the rate constant k, there-

fore $E_{A,eff}$ contains a contribution of the temperature dependence of the sorption processes. Since the observed reaction rate was plotted in the Arrhenius diagram, the calculated activation energy also contains the adsorption enthalpies of the reactants besides the activation energy of the surface reaction.

4 Conclusions

The commercial niobia hydrate (H. C. Starck) is a stable solid acid catalyst with relatively low activity in esterification reactions. Different approaches to increase the catalytic activity by modifications resulted in a lower activity than the original material already showed. The compressed pellets showed no mass transport limitations in the esterification of acetic acid with ethanol up to a particle diameter of 850 μm. Nevertheless, the compressing procedure and the resulting low porosity were found to be possible reasons for the low activity. Based on the results of a kinetic study a microkinetic model was proposed including two different kinds of active sites for the adsorption of ethanol and acetic acid, respectively. In contrast to conventional Langmuir/Hinshelwood and Eley/Rideal rate laws, this new model was the only one which could describe the reaction catalyzed by the investigated niobia hydrate. Protonated acetic acid is proposed as the reaction intermediate [8], and the mechanism is thereby similar to the homogeneous catalyzed esterification.

Table 3. Quality of fit of the four models.

Model	Stability index R^2
LH1	0.657
LH2	0.952
ER1	0.835
ER2	0.628

Symbols used

d	[m]	diameter
$E_{A,eff}$	[kJ/mol]	effective activation energy
k	[bar/s]	rate constant
K	[–]	reaction equilibrium constant
K_i	[bar^{-1}]	adsorption equilibrium constant
m_{Kat}	[g]	catalyst mass
n_i	[mol]	amount of substance
p_i	[bar]	partial pressure
r	[bar/s]	reaction rate
T	[K, °C]	temperature
$\dot{V}_l$	[m^3/s]	flow rate of liquid reactants
X		conversion
1		ethanol
2		acetic acid
3		water
4		ethyl acetate

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