Surface Reactions of Polyols in the Presence of Water

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Introduction
Due to the low vapour pressure of many biomass-derived oxygenates, aqueous phase processes are expected to play a key role in the production of renewable chemicals and fuels. The use of solid catalysts in these processes allows for facile separation. Consequently, it is not surprising that many recent publications described heterogeneously catalyzed processes in water including aqueous phase reforming, hydrogenolysis of polyols, dehydration of sugars, and aldol condensation. However, the lack of knowledge of the surface chemistry involved in these reactions limits the achievable selectivity, activity, and stability of many of these catalysts. Obtaining the needed insight into the surface chemistry of biomass-derived oxygenates is challenging because the low vapour pressure of most of these substances makes it very difficult to dose them into vacuum cells, which are used in traditional surface science studies. Consequently, new approaches have to be developed. In the present study, the surface chemistry of polyols on Al2O3, ZrO2, TiO2, CeO2, and Nb2O5 is elucidated using IR spectroscopy and DFT calculations.

Materials and Methods
γ-Al2O3 and TiO2 (anatase) were purchased from Sigma-Aldrich. ZrO2, CeO2, and Nb2O5 were prepared in-house. Prior to spectroscopic studies, the metal oxides were impregnated with aqueous solutions ethylene glycol, 1,2-propanediol, 1,3-propanediol, and glycerol. Free water was removed by storing the wet sample in a desiccator jar. Typically, the samples contained 1 wt% of the oxygenate. For IR studies, the impregnated oxides were pressed into self-supported wafers and placed in the high vacuum transmission IR cell. The first spectra were recorded under ambient conditions when the wafer still contained significant amounts of physisorbed water. Subsequently, the remaining water was removed at room temperature and 10−6 mbar. In some experiments, the temperature was increased to observe reactions of surface species. DFT calculations on the surface chemistry of glycerol were performed in VASP using the PBE-GGA exchange functional and the PAW method.

Results and Discussion
Aqueous phase adsorption isotherms of polyols on γ-Al2O3 showed that adsorption occurred, but to a lesser extent than on hydrophobic catalysts, such as zeolite ZSM-5 [1]. This shows that the oxygenates compete with water for adsorption sites on the surface. Upon interaction with γ-Al2O3, the C-O stretching bands in the IR spectrum of polyols shifted to higher wavenumbers indicating strong surface interactions, such as the formation of alkoxy bonds. In case of glycerol and 1,3-propanediol, the formation of alkoxy bonds was observed even when significant amounts of physisorbed water remained on the surface (Figure 1). However, ethylene glycol and 1,2-propanediol only formed such species when residual water was removed by evacuation. DFT calculations were performed to identify the most stable surface species formed from glycerol (Figure 2): Both primary alcohol groups strongly interact with a coordinatively unsaturated surface site on Al2O3 forming a multidentate alkoxy, whereas the secondary hydroxyl group forms a hydrogen bond with the surface. Only molecules with sufficient spatial separation between functional groups can form such a surface species. It was also shown that multidentate surface species effectively protect the surface of γ-Al2O3 against hydrolytic attack in hot liquid water [2]. Glycerol formed similar surface species on other metal oxides that contain strong Lewis acid sites (i.e. ZrO2, TiO2, CeO2, and Nb2O5) [3,4]. On ZrO2 and TiO2, co-adsorbed water and CO2 can prevent the formation of the hydrogen bond between the secondary alcohol group and a basic surface oxygen atom. The frequencies of C-O stretching vibrations of primary alcohol groups scaled linearly with the electronegativity of the metal atom providing an indication for reactivity trends in acid catalyzed reactions, such as dehydration. Direct dehydration of adsorbed glycerol on the Lewis acid sites of Nb2O5 yields hydroxyacetone as the main products, whereas acrolein is formed when Bronsted acid sites are involved in the conversion [4].

Significance
Polyols form multidentate surface species on metal oxide surfaces with strong Lewis acid sites. These surface species affect the stability [2] and selectivity [4] of metal oxide based catalysts for biomass conversion in aqueous phase. Similar surface interactions are important for waste water treatment [5].

References