Influence of alkaline metal on performance of supported silicotungstic acid catalysts in glycerol dehydration towards acrolein

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A B S T R A C T

A series of supported silicotungstic acid ($H_4SiW_{12}O_{40} \cdot xH_2O$) catalysts was prepared from selected silica and alumosilicate carriers. Alkaline metals lithium, potassium and caesium were added to modify catalyst Brønsted acidity. Physico-chemical characterisation of the catalysts was carried out with nitrogen adsorption (BET), X-ray diffraction (XRD), and infrared (IR) and Raman spectroscopy and revealed that the nature of the alkaline metal is significant for (i) specific surface area which rises with metal ion radii and (ii) dispersion of active compound formed from alkaline metal and silicotungstic acid on the support surface. Interestingly, acidic properties rather do not depend on nature of alkaline metal. The catalysts were catalytically evaluated at standardised reaction conditions in a continuous flow lab scale set-up (10 wt.% of glycerol in water, 225–300 °C, modified contact time 0.15 kg h mol^{-1}). Among the tested supported catalysts, lithium exchanged $H_4SiW_{12}O_{40} \cdot xH_2O$ showed highest activity and maximum selectivity of 70% for acrolein at complete conversion. Main effect of alkaline metal addition can be seen in improved selectivity and activity, in particular with silica supported catalysts.

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1. Introduction

During the last decade, commercialisation of biodiesel production from plant oils (triglycerides) on large scale caused a surplus of by-product glycerol on the chemicals market. Therefore, intensive research efforts are under way to find new outlets for glycerol either for chemical utilisation or energy generation. In particular, the work on chemical valorisation of glycerol by oxidation, hydrochlorination, esterification, oligomerisation and dehydration has led to promising results [1] and new processes have been realised very recently, e.g. Solvay S.A. commercialised the conversion of glycerol into epichlorohydrin by Epicerol® process [2,3].

Glycerol dehydration to acrolein is an attractive sustainable alternative to the conventional acrolein process that uses propylene stemming from petroleum. It is feasible even in the presence of a surplus of water. The reaction has been studied mostly with acidic catalysts over a broad range of reaction conditions covering liquid phase, gas phase and supercritical reaction regime. Among these catalysts were acids like H_2SO_4 and H_3PO_4 [4–7], metal phosphates [4,8–10], sulphates [11,12], oxides [11,13–15], zirconia based materials [16–20] and zeolites [11,21–25]. Also

heteropolyacids have been very recently evaluated by several research groups [11,26–30], in particular commercially available 12-heteropolyacids with Keggin structure; selectivities for acrolein above 70% have been reported. However, the major drawbacks of heteropolyacids being applied in heterogeneously catalysed gas phase reactions are the limited thermal stability [31] and their low specific surface area (1–5 m^2/g), in general.

Catalyst acidity is crucial for high acrolein yield, but leads mostly to a considerable loss in catalyst activity within few hours due to blocking of the surface by high-boiling deposits. Therefore, long-term catalyst evaluation is under intensive study [e.g. [32]]. The nature of the deposits is not clarified yet, because the raw material glycerol as well as the product acrolein is able to form various oligomers and polymers of different composition, respectively. However, some supported heteropolyacids like silicotungstic acid (HSiW) supported over alumina or alumosilicate showed higher tolerance for deactivation. Such catalyst showed slight deactivation over 100 h at 275 °C while selectivity for acrolein was nearly constant [27,32].

The removal of surface deposits with molecular oxygen (either fed periodically or permanently) could be an effective solution to overcome the limited catalyst lifetime in glycerol dehydration. First attempts have been reported for heteropolyacids use [27,33], WO_3/ZrO_2 [17,18,21,34], vanadium phosphorus oxide [35], NbO_2/SiO_2 [15] and $Nd_4(P_2O_7)_3$ [9]. In contrast, a very recent report claims the doping of heteropolyacid catalysts with noble metals and co-feeding of hydrogen during dehydration of glycerol leads to

improvement of long-term properties and thus, deactivation resistance [36].

Unfortunately, a subsequent oxidative removal of surface deposits usually requires temperatures around or above 500 °C and could therefore destroy heteropolyacid structures. This could be prevented to some extent by supporting the heteropolyacids on high surface metal oxides [37]. Larger pore size of the support also helps to slow down catalyst deactivation to some extent [27]. Nevertheless, nature of support and its textural properties have to be adjusted carefully. Silicotungstic acid ($H_4SiW_{12}O_{40} \cdot xH_2O$, HSiW) supported on γ-alumina proved to be among the most effective catalysts for gas phase dehydration of glycerol and acrolein selectivities above 70% at complete conversion have been reported [26,27]. The interaction of HSiW with alumina support seems to be stronger than with silica and leads to higher dispersion and thermal stability, as proved by TG/DTA studies [27]. Simultaneously, with the use of supports minor amount of heteropolyacid is necessary to get the same weight specific catalyst activity.

Another method to control the physicochemical properties of heteropolyacids can be established by exchange of protons by various alkaline metals in different concentrations [e.g. [36]]. The incorporation of K^+, Cs^+ and Rb^+ reduces water solubility and simultaneously increases specific surface area [38]. It has been reported that acidic HSiW promotes the condensation of formaldehyde and methyl formate to methyl glycolate and methyl methoxy acetate whereas completely cation exchanged compounds are inactive [39]. The activity of the heteropolyacid decreases in the same order as the electronegativity of incorporated alkaline metal increases. Salts of HSiW with alkaline metal cations being replaced by only one proton, e.g. $LiH_3SiW_{12}O_{40}$ or $Mg_{0.5}H_3SiW_{12}O_{40}$, show high activity in the above-mentioned reaction [40]. Similarly, the ammonium salt of tungstophosphoric acid $H_3PW_{12}O_{40}$ (HPW), unlike its parent acid, has high surface area due to its microporous structure; a high activity and product selectivity in the conversion of methanol to hydrocarbons was registered [41].

It is clear that the protons in the heteropolyacids are the source of catalyst activity because most of the completely cation exchanged salts were inactive in acid-base catalysis. The synthesis of non-stoichiometric K^+ or Cs^+ salts of HPW with a replacement ratio between two and three protons leads to solids with higher specific surface area compared to the parent heteropolyacid materials [42]. The highest activities in esterification of isoamyl alcohol were achieved upon substitution of 2.5 proton equivalents by Cs. The performance of this catalyst is attributed to its high surface area and its micro- and mesopores [43–45]. In general, addition of alkaline metals Cs or Rb provides good means to adjust simultaneously acidity and textural properties of silicotungstic acid [46]. In a recent paper, the use of a caesium exchanged HPW ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) for gas phase dehydration of glycerol was described for the first time [36]. The high initial acrolein yield dropped dramatically within few hours, but catalyst stability could be prolonged by addition of noble metals such as Ru, Pt or Pd.

We investigated the potential of alkaline metals Li, K and Cs to control the acidic properties of supported HSiW catalysts in glycerol dehydration. For a better understanding of their role, different synthesis methods (e.g. variation of sequence of preparation steps) were applied. Activity and acrolein selectivity were measured under variation of reaction temperature at first.

2. Experimental

2.1. Catalyst preparation

A series of catalysts with HSiW supported on alumosilicate and silica modified with Li, K and Cs was prepared by sequential incipient wetness impregnation. First, a measured amount of silicotungstic acid (*Fluka*; corresponding to 20 wt.% loading of final solid catalyst) was dissolved in the necessary volume of water and impregnated onto the proper mass of silica (*Fluka*; mean particle size 315–500 μm). Average pore diameter of the silica was 11 nm and the material therefore was denoted as S11. The suspension was stirred over night. Excess water was removed using a rotary evaporator at 40 °C and the solid precursors were dried at 120 °C in air for 2 h. After this, either lithium nitrate (*Merck*), potassium nitrate (*Acros*) or caesium nitrate (*Degussa*) was impregnated onto the dry precursor in a similar aqueous impregnation procedure. The solids were dried at 120 °C and finally calcined at 400 °C under airflow for 4 h. The stoichiometric ratio of alkaline metal and heteropolyacid was set to 1, i.e. 25% of the protons in $H_4SiW_{12}O_{40}$ might be replaced by alkaline metal atoms. A fourth sample was prepared following an inverted impregnation sequence, i.e. first Cs and second HSiW were added to the silica support (S11).

Another series of catalysts was prepared with alumosilicate support (Siral 20®, *Condea*; average pore diameter 5 nm, denoted as AS5), HSiW and nitrates of Li, K and Cs as described above.

The ready-made catalysts are denoted e.g. as Cs/HSiW/S11, indicating the preparation sequence as well as the nature of alkaline metal, heteropolyacid and support. The sample with inverted impregnation procedure is denoted as HSiW/Cs/S11.

2.2. Catalyst characterisation

BET surface area, pore volume and average pore diameter for the supports and supported heteropolyacid salts were obtained from nitrogen adsorption isotherms measured at −196 °C (*Micromeritics ASAP 2010*). Before the measurement, each sample was degassed at 200 °C for 4 h. The average pore diameters were calculated using the BJH method.

X-ray powder diffraction (XRD) measurements were carried out on a STADI P automated transmission diffractometer (*STOE, Darmstadt*) with CuKα[1] radiation and Ge monochromator. The pattern was scanned in the 2θ range of 5–60° (step width 0.5°, 100 s per step) and recorded with a STOE position sensitive detector. The samples were prepared to flat plates. Phase analysis was carried out with the *Win Xpow* software package, including the powder diffraction file (PDF).

Raman spectroscopic investigations were carried out using a fibre optical RXN-Spectrometer (*Kaiser Optical system, 785 nm Laser*) with a laser power of 50 mW.

IR spectroscopic studies using pyridine as probe molecule served for revealing acidic properties. Spectra were recorded with a *Bruker IFS 66* spectrometer equipped with a heatable IR cell with CaF_2 windows, connected to a gas dosing-evacuating system. The powdered samples were pressed to self-supporting wafers (diameter 20 mm, weight 50 mg). The samples were pre-treated in flowing 5%H_2/Ar at 350 °C for 1 h followed by cooling to ambient temperature. Then, pyridine was adsorbed for 1 h by directing an Ar stream through a pyridine-containing saturator. Physisorbed pyridine was flushed away by evacuating for 5 min at ambient temperature. Pyridine desorption was followed by heating under vacuum up to 350 °C. The infrared spectra were recorded in transmission mode with 2 cm^{-1} resolution and 100 scans. For all presented spectra, a background correction was made.

2.3. Catalytic tests

Test runs were carried out in a continuous flow setup (Fig. 1) with a glass tube reactor (length 14 cm, volume 35 ml) equipped with an internal guide tube for a thermocouple placed inside the catalyst bed. The reactor was mounted in an electrically heated tubular furnace. Catalyst particles were sized to 315–500 μm and