Ternary Me–P–Si oxides for catalytic conversion of biomass-derived chemicals: a closer look at the surface.

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Significance and Relevance

Silica based ternary catalysts with phosphorus and niobium, titanium or zirconium dispersed in the network have been prepared through an innovative one-pot sol-gel process. Their modulated acidity, due to different exposed surface sites, makes these materials promising candidates for heterogeneous catalysis in conversion of chemicals from biomasses, such as alcohols, ethers, saccharides. A systematic investigation of the surface properties of ternary Me–P–Si (Me = Nb, Ti, Zr) is here presented.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, Fundamental advances in understanding catalysis.
Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations.

Me-P_2O_5-SiO_2 mixed oxides are active solid catalysts for conversion of biomass-derived chemicals, whose surfaces show a complex distribution of active and adsorption sites depending on the support, the support modifications and the chemical nature of the metals. The tunable distribution of exposed Brønsted and Lewis acidic sites leads to catalysts that can coordinate and activate n-type bases, such as oxygenates compounds (alcohols, ethers, saccharides). The introduction of transition metals in a ternary oxide may deeply modify the distribution and strength of acid sites and thus the catalytic performances. In a previous work, Nb-P-Si catalysts has been synthesized by sol-gel route and tested in different reactions, such as ethanol dehydration and diethylether conversion. Results were encouraging in view of applications in industrial chemistry[1,2,3]. Very recently, we undertook an extensive investigation of surface properties of Ti-P-Si and Zr-P-Si ternary systems, synthetized by a one-pot hydrolytic sol-gel route, to be compared to the previous reference formulation Nb-P-Si. The alternative approach adopted in the synthesis of Ti-P-Si and Zr-P-Si ternary materials, with respect to the traditional ones, such as grafting or impregnation, has allowed to obtain the formation of a homogeneous dispersion of the active phase into the siloxane matrix[4]. In this work a thorough investigation on the nature and the amount of exposed acidic sites together with catalytic data on sucrose conversion, as test reaction, are reported. The issue of the stability of the catalysts in demanding conditions is also addressed.

Materials and Methods.

The ternary oxides were synthesized by the hydrolytic sol-gel route described in detail in refs. 3 and 4, using H_3PO_4 as P precursor, ammonium niobium oxalate as Nb precursor and alkoxides as Zr, Ti and Si precursors, keeping Me/P atom ratio equal to 2. Nominal molar compositions of MePSi materials considered here are: $5Nb_2O_5 \cdot 2.5P_2O_5 \cdot 92.5SiO_2$ (NbPSi), $10TiO_2 \cdot 2.5P_2O_5 \cdot 87.5SiO_2$ (TiPSi) and $10ZrO_2 \cdot 2.5P_2O_5 \cdot 87.5SiO_2$ (ZrPSi). One binary P_2O_5-SiO_2 (PSi) sample, as well as the pure support silica, were also synthesized as reference. The resulting materials have been characterized by TGA, XRD, BET. Acid site number was quantified by gas-solid titrations by NH_3 probe adsorption in flowing dynamic experiments and by pyridine probe molecule adsorption in situ FT IR studies, both on dry and on hydrated surfaces. Residual acidity was also evaluated by probe molecules adsorption over samples submitted to water pretreatment.

Results and Discussion

The surface chemistry of silica materials is driven by the exposed silanol groups, which show a weak protonic acidity. The modification with phosphorus and niobium leads to the appearance of Brønsted acid sites[3], while Me addition also introduces a medium-weak Lewis acidity, associated to the presence of exposed coordinatively unsaturated Zr and Ti ions. Likely, the presence of electron-withdrawing atoms also affects acidity of the nearby silanol groups. Over the fully hydroxylated surface the same type of sites, that is weak and Brønsted protonic sites and Lewis sites is detected, the latter at a slightly lower extent (Figure 1,a and b). Possibly, Lewis sites are more evident in the spectrum of ZrPSi sample, in agreement with XPS results pointing out a relative enrichment of this metal sites at the catalyst surface[4]. N_2 adsorption-desorption isotherms reveal the microporous nature of MePSi samples. Comparing the effect of Ti and Zr modifications, slightly higher surface area values for TiPSi (395 ± 11 m^2/g) than ZrPSi (346 ± 37 $m^2\ g^{-1}$) were reported, while the two samples show similar pore volumes (ca. 0.2 $cm^3\ g^{-1}$) and pore size distributions dominated by small micropores. The total number of acid sites was titrated using ammonia as a basic probe molecule: TiPSi and ZrPSi showed similar acid character with similar acid site density (about 1.7 μeq m^{-2})[4].

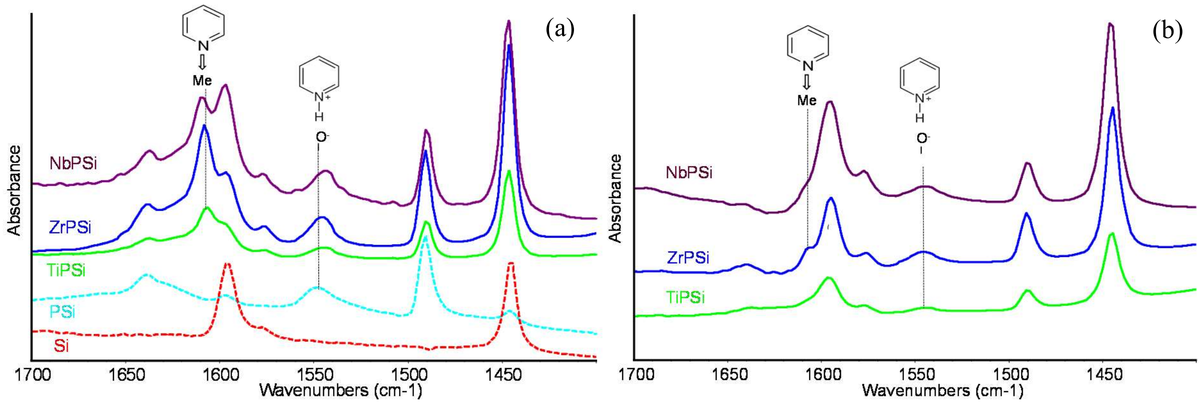

Figure 1. FT IR subtraction spectra of pyridine adsorbed and desorbed at 150 °C over Nb, Ti, Zr ternary systems: (a) partially dehydroxylated surface, (b) highly hydroxylated surface. The spectrum of the corresponding activated surface has been subtracted.

It is possible to suggest that the acid character of the surfaces is mainly ascribable to surface hydroxy groups, either Si–OH (whose acidity might be enhanced by nearby metal ions), and P–OH groups, in agreement with FTIR data of adsorbed pyridine[4]. Preliminary catalytic data on the hydrolysis of sucrose confirmed the activity of Zr and Ti based catalysts, also indicating a faster reaction rate over the Ti-P-Si ternary oxide. Surface studies are now in progress on the modification of these catalysts eventually occurring after pretreatments in harsh conditions.

References

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