Development of acidic sites in WO$_x$/ZrO$_2$

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Evidence is shown of the appearance of Brønsted acidic sites in WO$_x$/ZrO$_2$ at a given W loading and of a direct correlation between the abundance of 'strong' Brønsted acidic sites in these catalysts and propan-2-ol decomposition activity.

It is well established that addition of W onto zirconia induces the formation of acid sites. With suitable preparation methods solid acid catalysts can be obtained which can isomerise *n*-hexane.[1] However, the genesis of acidity and the actual nature of the acid sites have not been fully investigated. Previous work with WO$_x$/ZrO$_2$ obtained by the incipient wetness impregnation method, indicated that a threshold of W loading was required for any activity for propan-2-ol decomposition to develop.[2] Similar behaviour was already reported for solids obtained by impregnation of zirconium hydroxide, for different reactions such as *o*-xylene[3] and *n*-pentane[4,5] isomerisation. It was proposed,[2] but not verified, that the origin of this behaviour is due to the formation of different types of acid sites at a given W loading. Furthermore, the simultaneous presence of polymeric surface WO$_x$ and bulk WO$_3$ in active catalysts complicated any attempt to elucidate the nature of the active sites.

In the present work, a series of WO$_x$/ZrO$_2$ catalysts was prepared by the equilibrium adsorption method.[6] This procedure was shown to prevent WO$_3$ formation. A direct correlation between the surface structure and the catalytic activity for propan-2-ol decomposition is reported.

Tungsten surface species were monitored by Raman spectroscopy. The number, the strength and the type of acidity were characterised by IR spectroscopy. Propan-2-ol decomposition was used as a probe reaction to assay the acidity of the solids.

Catalysts were prepared by adsorption of W from aqueous solutions of ammonium metatungstate on zirconia (ZrO$_2$).[6] The support was prepared by hydrolysis of zirconium *n*-propoxide [Zr(OPr)$_4$, 70% in *n*-propanol; Aldrich]. The precipitate thus obtained was washed free of propanol, dried and calcined at 823 K in air for 24 h.[7] The original zirconia had a BET surface area of 43 m^2 g^{-1}. A series of WO$_x$/ZrO$_2$ catalysts was prepared by suspending a known amount of ZrO$_2$ in a large volume of aqueous ammonium metatungstate solution [(NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$, Aldrich] at a given pH. The samples were filtered off, dried and calcined at 773 K in air for 24 h. Solids with various W loadings ranging from 1.1 to 4.6 wt% W were obtained by modifying either the pH of the adsorption solution (adsorption time = 96 h) or the adsorption time (at pH = 12). No significant surface area loss was observed on W deposition.

Raman spectra were recorded with a Nicolet FT-Raman spectrometer attachment for a Nicolet Nexus FTIR spectrometer between 100 and 1100 cm^{-1} (resolution: 8 cm^{-1}). The samples were analysed in powder form and under ambient conditions without any pre-treatment. The technique was used to monitor the structure of the support (monoclinic; tetragonal), WO$_3$ formation and the evolution of surface W species.

IR spectra were recorded with a Nicolet 710 FT-IR spectrometer (resolution: 4 cm^{-1}). Samples were pressed into discs (*ca.* 20 mg; 2 cm^2) and activated alternatively in vacuum and O$_2$ at 723 K. Acidic properties (type and abundance) of the samples were characterised by two basic probe molecules (CO and 2,6-dimethylpyridine). CO was introduced at room temperature by doses (from 2.6 to 664 µmol g^{-1}) up to an equilibrium pressure of 133 Pa. 2,6-dimethylpyridine (lutidine) was introduced at room temp. ($P_{equilibrium}$ = 133 Pa) followed by thermodesorption from 373 to 573 K.

The catalytic conversion of propan-2-ol was measured in a fixed bed flow reactor. A mass of 100 mg of sample was pre-treated at 723 K in N$_2$ for 2 h. The reaction was carried out at atmospheric pressure with 120 ml min^{-1} N$_2$ as carrier gas ($P_{propan-2-ol}$ = 1.23 kPa) at 413 K. Reactants and products were analysed with an on line Gas Chromatograph (HP 5890 Serie II) equipped with a capillary column (CP WAX 52 CB) and an FID detector. Catalytic study was conducted in non diffusional conditions, with conversions typically below 10%. Neither an induction period nor deactivation were observed during the analysis time (2 h). The rate of propene formation was calculated from eqn. (1), assuming a first order reaction for propan-2-ol:

$$r = -\frac{F_0}{W}\ln\left(\frac{100-C}{100}\right) \quad (1)$$

where *r* is the rate of propene formation (mol h^{-1} g^{-1}), F_0 is the propan-2-ol molar flux (mol h^{-1}) and *C* is the % conversion to propene.

Raman spectra of WO$_x$/ZrO$_2$ catalysts and the zirconia support showed intense peaks between 100 and 700 cm^{-1} characteristic of the monoclinic phase of zirconia.[8] No Raman peaks which can be ascribed to bulk WO$_3$ were detected.[9] A band at 935 cm^{-1} attributed to the W surface phase appears on W deposition and increases in intensity with W loading. A shift in the position of this band to higher wavenumbers is observed with W content in accordance with previous results.[10] This is indicative of monomeric to polymeric transformation of W species.

The IR spectra of tungstated zirconias show significant dehydroxylation which increases with W loading. This indicates that W deposition occurs *via* replacement of the hydroxyl groups.

The presence of Lewis acid sites was monitored by FTIR and CO adsorption. The amount of CO required to saturate the sites decreased on W addition but it remained the same for all the tungstated solids.

The adsorption of lutidine at room temp. followed by evacuation at 423 K evidenced the presence of Brønsted acidic sites on the surface of WO$_x$/ZrO$_2$ catalysts. This is illustrated in Fig. 1(a) by the appearance of a doublet at 1645 and 1628 cm^{-1} attributed to lutidinium species and the subsequent increase of its intensity with increasing W loading. The peaks at 1610 and 1580 cm^{-1} are attributed to Lewis acid sites. After desorption of lutidine at 423 K, Brønsted acid sites were still observed for a W loading of 1 atom nm^{-2}. However, following desorption at 523 K only the Brønsted acid sites of solids containing more than 1.4 atom W nm^{-2} were sufficiently strong to retain the probe molecule on the surface [Fig. 1(b)]. These results are comparable to those reported by Wachs[11] concerning the appearance of Brønsted acidity on molybdenum, vanadium and niobium oxide supported on alumina.

The catalysts were tested for the reaction of propan-2-ol decomposition. Only two products, propene and diisopropyl ether were observed. For all catalysts, the selectivity to propene was high (≥ 85%) and increased with temperature as expected
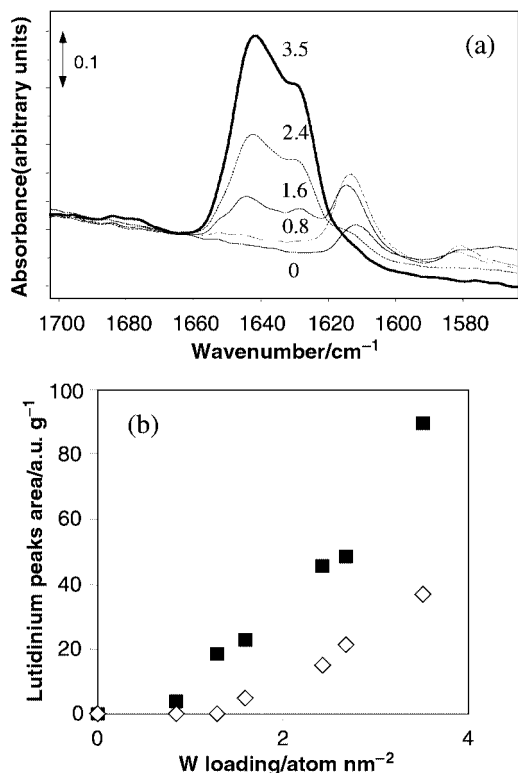
Fig. 1 Evolution of the lutidinium band. (a) IR spectra of lutidine evacuated at 423 K. (b) Evolution of the area of the band (1620–1660) after desorption of lutidine at 423 K (■) and 523 K (◇). [Numbers in (a) refer to the W loading in W atom nm^{-2}].

from thermodynamics. These results are consistent with acid catalysis.[7] In Fig. 2 the rate of propene formation was plotted *vs.* W content. The results show a very low rate up to 1.4 atom W nm^{-2}, followed by a steep increase for higher loadings. Similar behaviour was observed for measurements performed with different flows and temperatures. Fig. 2 compares the evolution of catalytic activity with that of the intensity of lutidinium band. Note that the onset of catalytic activity coincides with the appearance of 'strong' Brønsted sites. In addition, the evolution of the rate of decomposition parallels that of the abundance of Brønsted acid sites. The decomposition of propan-2-ol appears, thus, directly related to the presence and abundance of 'strong' Brønsted acid sites. Note that in the present study Brønsted acid sites are formed *prior* to any reductive treatment. This is in variance with previous studies[12] where strong Brønsted acid sites were reportedly formed on reduction of WO_x clusters in H_2 or by the reactant mixture. The appearance and the evolution of the abundance of the Brønsted sites on our catalysts suggest that
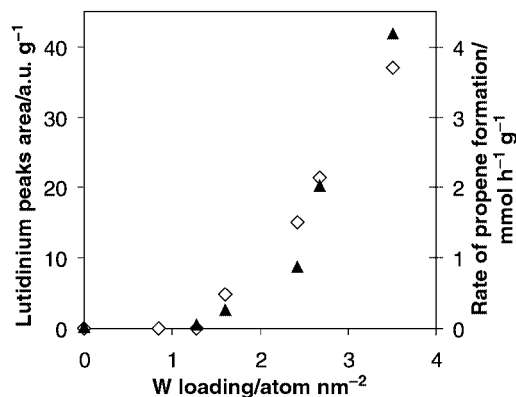

Fig. 2 Correlation between propene formation rate (▲) and abundance of "strong" Brönsted sites as evidenced by lutidinium peaks area after desorption at 523 K (◇).

a minimum degree of polymeric WO_x units may be necessary for the formation of acidic sites. A similar behaviour was observed for WO_x/Al_2O_3 catalysts and was attributed to an enhanced stabilisation of the proton by delocalisation among adjacent W atoms.[13,14] This interpretation is consistent with the observed lack of activity for low loading catalysts where W is reportedly present in a monomeric form. These results highlight the importance of extended W coverage for the development of Brønsted acid sites on supported catalysts.

Notes and references

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