

# Study of acidic commercial $\text{WO}_x/\text{ZrO}_2$ catalysts by adsorption microcalorimetry and thermal analysis techniques

R. Kourieh · S. Bennici · A. Auroux

MEDICTA2009 Conference  
© Akadémiai Kiadó, Budapest, Hungary 2009

**Abstract** In this work we report about the characterization of the acidic and redox properties of four different commercial tungstated zirconia catalysts with W loadings of about 12–13 mass%. The samples have been characterized in terms of their micro-structural and surface properties by BET, X-ray diffraction, temperature programmed reduction, elemental chemical analysis and adsorption microcalorimetry of  $\text{NH}_3$ . Improved acidity has been detected upon addition of  $\text{WO}_3$  to zirconia and differences between the samples were pointed out thanks to the results obtained by the complementary physico-chemical techniques used in this study.

**Keywords** Tungsten oxide · Zirconia supported catalysts · Surface acidity · Adsorption microcalorimetry

## Introduction

Tungstated zirconia ( $\text{WO}_x/\text{ZrO}_2$ ) has received considerable attention due to its potential catalytic application in hydrocarbon conversion reactions in the petrochemical industry [1–4].

The challenge to obtain solid acid catalysts with acid sites of comparable strength to those in sulfuric acid is still open in an attempt to eliminate environmental concerns caused by the use, regeneration, transportation and storage

of liquid acids [5]. Moreover, in the last years the growing interest towards biodiesel, a clean fuel source which is viewed as a viable alternative for dwindling petroleum-based diesel resources, has led to renewed interest in acid catalysts [6]. Better yet, if solid acid catalysts could replace liquid acids, the corrosion and environmental problems associated with them could be avoided and product purification protocols could be significantly reduced, simplifying various hydrocarbons transformation reactions, and thus reducing their costs. Moreover heterogeneous catalysts are preferable because offering easy separation from the reactants and products which are either liquids or gases.

It is known that catalytic activity of oxides can be related to the cooperative action of an oxidizing function and an acidic function. From this perspective, the determination of both redox and acidic properties of the catalytic centers becomes of fundamental importance in the present study.

Adsorption of a basic probe molecule ( $\text{NH}_3$ ) will be used in adsorption calorimetry, one of the most powerful techniques for the determination of the number, strength and strength distribution of surface acid sites of catalysts [7]. Besides the redox character will be determined using thermoprogrammed reduction and oxidation experiments.

## Experimental

Four tungstated zirconia supported catalysts (labeled XZO-1903-1, XZO-1903-2, XZO-1903-3, XZO-1251-01) and a  $\text{Zr}(\text{OH})_4$  support (ZO), supplied by MEL-Chemicals, have been calcined at 700 °C under air flow for 4 h.

Elemental analysis was performed using ICP atomic emission spectroscopy (ICP-AES) with a flame Perkin-Elmer M1100 spectrometer.

R. Kourieh · S. Bennici · A. Auroux (✉)  
CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Université Lyon 1, 2 Avenue Albert Einstein, 69626 Villeurbanne, France  
e-mail: aline.auroux@ircelyon.univ-lyon1.fr

The surface areas and pore sizes were measured by nitrogen adsorption at  $-196\text{ }^{\circ}\text{C}$  on a Micromeritics 2010 apparatus after heat pretreatment under vacuum for 2 h at a temperature of  $400\text{ }^{\circ}\text{C}$ .

The X-ray diffraction (XRD) measurements were carried out on a Bruker D5005 powder diffractometer scanning from  $3^{\circ}$  to  $80^{\circ}$  ( $2\theta$ ) at a rate of  $0.02^{\circ}\text{ s}^{-1}$  using a Cu  $K\alpha$  radiation ( $\lambda = 0.15418\text{ nm}$ ) source. The applied voltage and current were 50 kV and 35 mA, respectively.

The thermogravimetric (TG) analyses were performed on a SETARAM Labsys instrument in the 303–1,073 K temperature range, with a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$ , under air flow.

Temperature programmed reduction and oxidation experiments were performed using a TPD/R/O-1100 instrument (Thermo). Redox cycles (TPR/TPO/TPR2) were realized carrying out sequentially a temperature programmed reduction (TPR1) on the oxidized sample followed by a temperature programmed oxidation (TPO) and then a second temperature programmed reduction (TPR2). The samples were initially pre-treated in  $\text{O}_2/\text{He}$  flow ( $20\text{ mL min}^{-1}$ ) at  $350\text{ }^{\circ}\text{C}$  for 60 min. After cooling to room temperature, the  $\text{H}_2/\text{Ar}$  (4.96% v/v) reducing mixture flowed through the sample at  $20\text{ mL min}^{-1}$  with the temperature increasing from 40 to  $700\text{ }^{\circ}\text{C}$  at a rate of  $10\text{ }^{\circ}\text{C/min}$ . TPO run was carried out on the reduced sample cooled at  $40\text{ }^{\circ}\text{C}$  in  $\text{H}_2/\text{Ar}$  flow. After Ar purge ( $10\text{ mL min}^{-1}$ ), the  $\text{O}_2/\text{He}$  (0.99% v/v) oxidizing mixture flowed at  $20\text{ mL min}^{-1}$  through the sample with similar experimental conditions, in terms of temperature increasing and range, to those used for TPR analysis. On the re-oxidized sample a second reduction (TPR2) was performed in the same conditions as TPR1 but increasing the temperature up to  $1,000\text{ }^{\circ}\text{C}$  instead of  $700\text{ }^{\circ}\text{C}$ .

Ammonia ( $\text{p}K_{\text{a}} = 9.24$  and PA (proton affinity) =  $857.7\text{ kJ mol}^{-1}$ ), dried on 3A zeolite spheres, was used as a basic probe molecule to titrate the surface acid sites of the samples. Calorimetric and volumetric gas–solid titrations were carried out concomitantly in a volumetric line linked to a heat-flow microcalorimeter (Tian-Calvet type, C80 from Setaram). The chosen adsorption temperature was  $80\text{ }^{\circ}\text{C}$  to limit physisorption. About 0.1 g of powder sample previously calcined at  $700\text{ }^{\circ}\text{C}$  was pretreated under vacuum at  $400\text{ }^{\circ}\text{C}$  overnight (about 12 h) and then evacuated at the same temperature for 1 h prior to the measurements. Small successive  $\text{NH}_3$  injections were sequentially sent onto the sample, up to a final  $\text{NH}_3$  pressure of about 60 kPa. The equilibrium pressure relevant to each adsorbed amount was measured by means of a differential Barocel capacitance manometer (Datametrics). At the end of the adsorption, a second adsorption was performed after desorption (1 h at  $80\text{ }^{\circ}\text{C}$ ) of the  $\text{NH}_3$  amount weakly retained on the surface. The difference between the first and second isotherms at

$27\text{ kPa}$  represented the strongly chemisorbed  $\text{NH}_3$  amount, the so-called irreversible amount ( $V_{\text{irr}}$ ).

## Results and discussion

More or less significant differences in the surface properties between the  $\text{WO}_3$  containing catalysts and the bare  $\text{ZrO}_2$  support emerged from the various techniques used for characterizing the samples.

The chemical analysis values (expressed as W mass%) and the BET surface areas (in  $\text{m}^2\text{ g}^{-1}$ ) of the zirconium-tungsten mixed oxides as well as of the zirconia are presented in Table 1. The tungsten amount was always close to 12–13 mass% which is slightly above the monolayer coverage (10.7 mass%) [8] assuming a surface concentration of tungsten of  $3.5\text{ W-atom-nm}^{-2}$  for the monolayer. Even after calcination at  $700\text{ }^{\circ}\text{C}$  the catalysts maintained a remarkable surface area (between  $80$  and  $105\text{ m}^2\text{ g}^{-1}$ ), while the bare calcined zirconia decreased its surface down to  $37\text{ m}^2\text{ g}^{-1}$ .

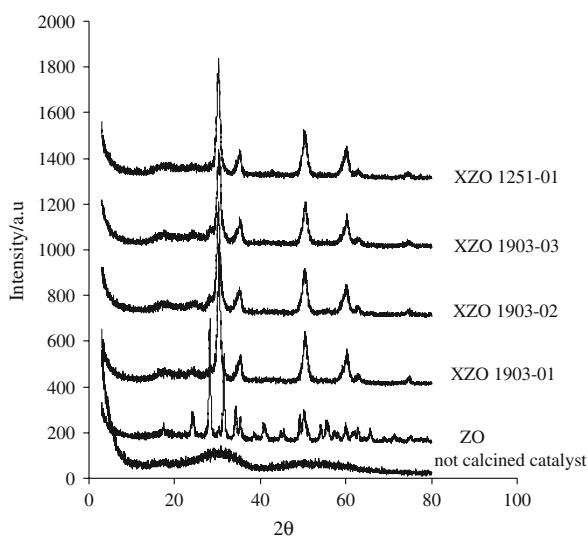
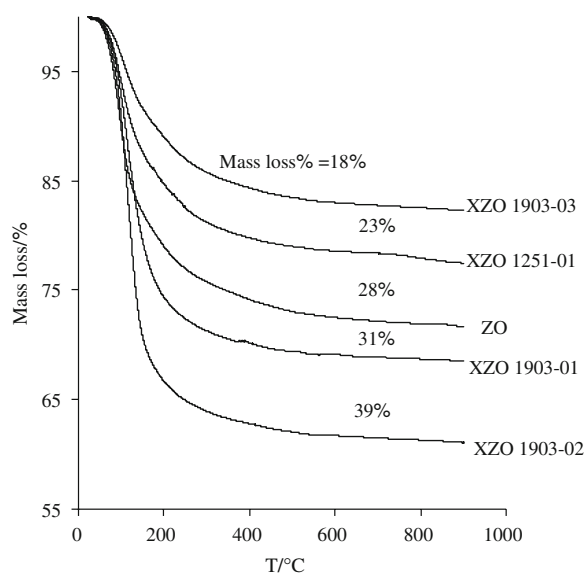
The XRD patterns of the un-calcined samples as received from Mel Chemicals (Fig. 1) show the same amorphous phase (for this reason only one sample is shown). The calcination of the catalysts at  $700\text{ }^{\circ}\text{C}$  resulted in the appearance of the tetragonal  $\text{ZrO}_2$  phase only, as shown by the X-ray diffractograms reported in Fig. 1. At the same calcination temperature, the ZO support gave rise to the well known segregation into a mixture of tetragonal and monoclinic  $\text{ZrO}_2$  with the specific reflections of the monoclinic phase at  $28.3^{\circ}$  and  $31.6\text{ }2\theta$  [9–11]. It is known that at a given W concentration, the BET surface area and the tetragonal content in  $\text{ZrO}_2$  decrease with calcination temperatures higher than  $500\text{ }^{\circ}\text{C}$  [12]. The presence of  $\text{WO}_x$  species in fact inhibits the sintering and the transformation to monoclinic  $\text{ZrO}_2$  crystallites, as demonstrated from the XRD and BET results of the four samples containing W. Moreover, no specific diffraction peak of  $\text{WO}_3$  crystallites ( $2\theta = 23.2^{\circ}$ ,  $23.7^{\circ}$ , and  $24.3^{\circ}$ ) has been detected in any of the catalysts.

TG analyses were carried out to provide information about any decomposition of the sample and also to help in determining a more accurate calcination temperature of the un-calcined samples.

Typical TG curves of the materials before calcination are shown in Fig. 2. All samples showed basically one event of mass loss that can be attributed to the releasing of physisorbed and structural water molecules. The decomposition of the precursor (mostly  $\text{Zr}(\text{OH})_4$ ) occurred mainly between  $70$ – $500\text{ }^{\circ}\text{C}$ , with a mass loss which could attain up to the 39% of the initial mass. The residue at  $700\text{ }^{\circ}\text{C}$  corresponds essentially to  $\text{WO}_x/\text{ZrO}_2$  oxides, as shown by chemical analysis and XRD.

**Table 1** Physicochemical characteristics of pure zirconia and tungstated zirconia catalysts

Sample	W content/ mass%	BET surface area/m <sup>2</sup> g <sup>-1</sup>	Acidity		
			$Q_{\text{init}}/\text{kJ mol}^{-1}$	$V_{\text{tot}}/\mu\text{molNH}_3 \text{ g}^{-1}$	$V_{\text{irr}}/\mu\text{molNH}_3 \text{ g}^{-1}$
XZO- 1903-01	12.2	88	180	234	147
XZO- 1903-02	12.6	101	158	291	199
XZO- 1903-03	12.3	111	175	321	214
XZO- 1251-01	13.2	105	170	285	173
ZO	–	37	178	124	68

**Fig. 1** XRD of WO<sub>x</sub>/ZrO<sub>2</sub> commercial catalysts calcined at 700 °C, un-calcined, and of the bare ZrO<sub>2</sub>**Fig. 2** TG curves of the un-calcined catalysts and zirconium hydroxide

The water loss due to the thermal treatment of the manufactured samples caused several changes in the zirconia which means decreasing surface area and formation of

crystallites. Upon analysing the TG curves the decision to calcine all catalysts at 700 °C has been taken with the aim to remove most of the OH groups physically or chemically adsorbed on the surface, to decompose any precursor eventually still present, and to facilitate the adhesion and condensation of tungstate species on the ZrO<sub>2</sub> surface [13].

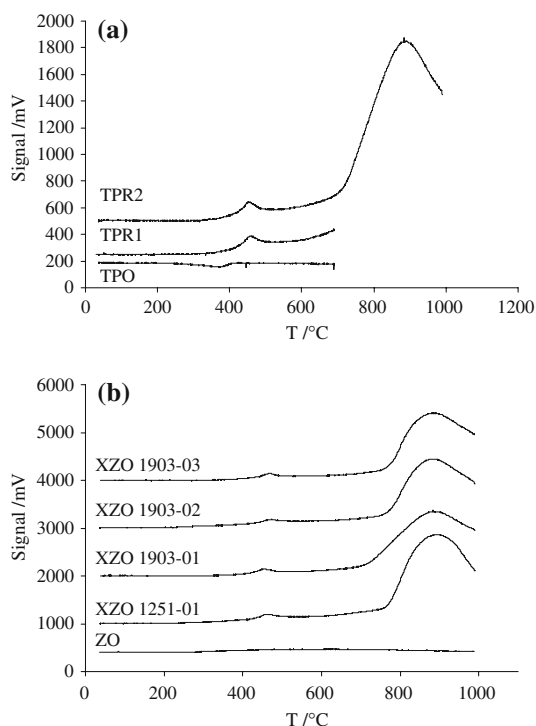
To verify the existence of species capable to participate in a red-ox cycle TPR/TPO/TPR2 analyses have been performed (see Fig. 3a) as described in the experimental section. A first reduction (TPR) has been carried out up to a maximum temperature of 700 °C, corresponding to the calcination temperature required to avoid structural changes in the catalyst structure before to achieve the red-ox cycle. TPR1 analysis showed for all the catalysts a reduction peak centered around 460 °C, that was completely re-oxidized during the TPO treatment and that could be attributed to the reduction of WO<sub>3</sub> crystallites, too small to be revealed by XRD.

The WO<sub>3</sub> species reduced at 460 °C can be re-oxidized and again reduced as evidenced by the reduction peak present in the TPR2 curve at the same temperature. In the TPR2 analysis, presented in Fig. 3b, the temperature was increased up to 1,000 °C. The TPR2 curves exhibited a broad reduction peak with a maximum temperature centered around 880 °C, which can be related to the reduction of tetrahedrally coordinated species anchored to the zirconia [14].

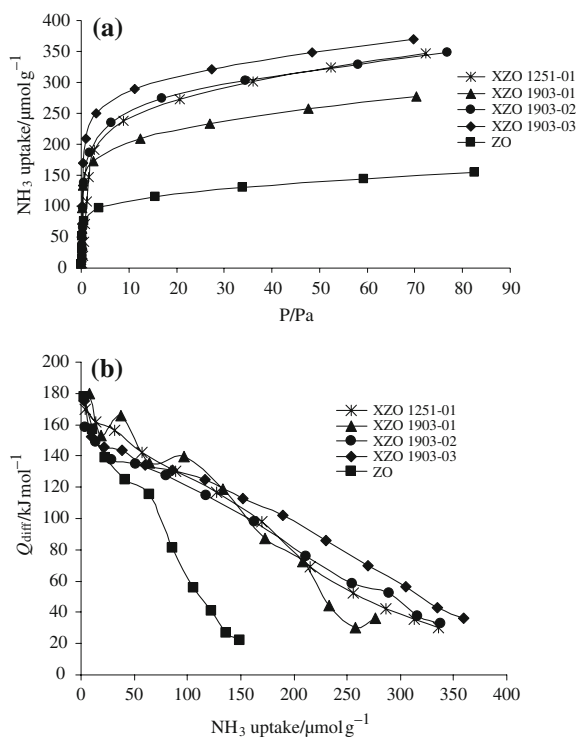
Because the XRD results did not indicate the presence of WO<sub>3</sub> crystalline structure, we can assume that the broad peak detected at temperature higher than 700 °C is related to the reduction of WO<sub>x</sub> species (amorphous and non-stoichiometric oxides) strongly anchored to the support. No quantitative evaluation of the amount of H<sub>2</sub> consumed was done due to the experimental conditions (TPR2  $T_{\text{max}} = 1,000^\circ\text{C}$ ) that did not allow to complete the high temperature peak.

The amounts of NH<sub>3</sub> adsorbed at 80 °C and the corresponding interaction energies with the bare ZO sample and the tungstated zirconia catalysts were determined by means of a volumetry–calorimetry coupled technique.

The equilibrium isotherms and differential heats of NH<sub>3</sub> adsorption are reported in Fig. 4a and b, respectively.



**Fig. 3** a TPR1/TPO/TPR2 profiles for the XZO-1903-02 catalyst and b TPR2 profiles for the catalysts and zirconia



**Fig. 4** a Ammonia adsorption isotherms and b differential heats of ammonia adsorption vs. coverage at 80 °C on WO<sub>3</sub>/ZrO<sub>2</sub> catalysts and pure ZrO<sub>2</sub> calcined at 700 °C

The volumetric adsorption isotherms of the studied samples displayed in all cases an initial vertical section proportional to the amount of strongly chemisorbed NH<sub>3</sub> [15]. The heats of adsorption showed a decreasing trend upon increasing coverage, as usually observed for heterogeneous surfaces [7, 16, 17]. For WO<sub>x</sub>/ZrO<sub>2</sub> catalysts the contribution from Lewis acidity may be influenced by the nature of the second oxide. The heterogeneity of the studied materials is due to the presence of acidic sites of different natures (i.e. Lewis acid sites from WO<sub>x</sub> and both Brønsted and Lewis sites from zirconia) and presenting various strengths [18]. The tungsten oxide catalysts showed a higher capacity to adsorb NH<sub>3</sub>, if compared to pure ZrO<sub>2</sub>.

According to its adsorption properties towards NH<sub>3</sub> and CO<sub>2</sub>, tungsten oxide was classified as acidic oxide while zirconia was assigned to the amphoteric group [19]. However, it was found that many oxides in the amphoteric group adsorbed more NH<sub>3</sub> and with a higher heat than some of the ones in the acidic group. Also the ZrO<sub>2</sub> sample adsorbed NH<sub>3</sub> with a heat of 150 kJ mol<sup>-1</sup>, comparable to WO<sub>3</sub> [19]. Depending in their preparative procedures zirconia samples can display very different adsorption heats [20]. It should be noted that in the case of pure zirconia, the smaller surface area associated to our sample suggests a more complicated picture in ranking solid acids.

The slight increase in the total number of acid sites and the small decrease in the initial heat when going from sample XZO-1901-01 to sample 03 might be related to a difference in history and aging as they are issuing from the same initial batch.

Moreover our results are very comparable to those obtained by Vartuli et al. [21] who reported a total acidity of 308 μmol<sub>NH<sub>3</sub></sub> g<sup>-1</sup>, an initial heat of 155 kJ mol<sup>-1</sup> and an overall average integral heat of adsorption of 107 kJ mol<sup>-1</sup> for a WO<sub>x</sub>/ZrO<sub>2</sub> catalyst prepared by coprecipitation (62 m<sup>2</sup> g<sup>-1</sup>, 15.9 W mass%) and calcined at 700 °C.

## Conclusions

Coupling WO<sub>x</sub> species with ZrO<sub>2</sub> gives rise to improved materials both in terms of surface acidity and structure stability. The loss of surface area of pure zirconia is significantly inhibited by the presence of WO<sub>x</sub> species. A calcination at 700 °C has been shown to be high enough to ensure the complete elimination of the synthesis precursor as well as the physisorbed and structural water, and low enough to avoid the sintering of the WO<sub>x</sub> crystallites.

The combination of different thermal, calorimetric and structural analysis has permitted to deeply analyze samples that can be potentially applied as acidic catalysts in different environmental friendly reactions such as biodiesel-forming transesterifications.

## References

1. Kim T, Burrows A, Kiely CJ, Wachs IE. Molecular/electronic structure—surface acidity relationships of model supported Tungsten oxide catalysts. *J Catal.* 2007;246:370–81.
2. Wachs IE, Kim T, Ross EI. Catalysis science of the solid acidity of model supported Tungsten oxide catalysts. *Catal Today.* 2006;116:162–8.
3. Busca G. Acid catalysts in industrial hydrocarbon chemistry. *Chem Rev.* 2007;107:5366–410.
4. Ji W, Hu J, Chen Y. The structure and surface acidity of zirconia-supported tungsten oxides. *Catal Lett.* 1998;53:15–21.
5. Kogelbauer A, Vassena D, Prins R, Armor J. Solid acids as substitutes for sulfuric acid in the liquid phase nitration of toluene to nitrotoluene and dinitrotoluene. *Catal Today.* 2000;55:151–60.
6. Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JG. Synthesis of biodiesel via acid catalysis. *Ind Eng Chem Res.* 2005;44:5353–63.
7. Bennici S, Auroux A. Thermal analysis and calorimetric methods. In: Jackson SD, Hargreaves SJ, editors. *Metal oxide catalysis.* : Wiley-VCH Verlag GmbH & Co; 2009. p. 391–442.
8. Naito N, Katada N, Niwa M. Tungsten oxide monolayer loaded on zirconia: determination of acidity generated on the monolayer. *J Phys Chem B.* 1999;103:7206–13.
9. Di Gregorio F, Keller V. Activation and isomerization of hydrocarbons over WO<sub>3</sub>/ZrO<sub>2</sub> catalysts: I. Preparation, characterization, and X-ray photoelectron spectroscopy studies. *J Catal.* 2004;225:45–55.
10. Arata K. Preparation of superacids by metal oxides for reactions of butanes and pentanes. *Appl Catal A Gen.* 1996;146:3–32.
11. Kuba S, Concepcion Heydorn P, Grasselli RK, Gates BC, Che M, Knozinger H. Redox properties of tungstated zirconia catalysts: relevance to the activation of n-alkanes. *Phys Chem Chem Phys.* 2001;3:146–54.
12. Barton DG, Soled SL, Iglesia E. Solid acid catalysts based on supported tungsten oxides. *Top Catal.* 1998;6:87–99.
13. Garrido Pedrosa AM, Souza MJB, Melo DMA, Araujo AS. Thermo-programmed reduction study of Pt/WO<sub>x</sub>-ZrO<sub>2</sub> materials by thermogravimetry. *J Therm Anal Calorim.* 2007;87:351–5.
14. Garrido Pedrosa AM, Souza MJB, Lima SH, Melo DMA, Souza AG, Araujo AS. Influence of the synthesis method on the DTG-TPR profiles of Pt/WO<sub>x</sub>-ZrO<sub>2</sub> bifunctional catalysts. *J Therm Anal Calorim.* 2007;87:703–7.
15. Sprinceana D, Caldararu M, Ionescu NI, Auroux A. Calorimetric study of the acidity and interface effects of tin dioxide layers deposited on another metal oxide. *J Therm Anal Calorim.* 1999;56:109–15.
16. Auroux A. Acidity characterization by microcalorimetry and relationship with reactivity. *Top Catal.* 1997;4:71–89.
17. Busco C, Barbaglia A, Broyer M, Bolis V, Foddanu GM, Ugliengo P. Characterisation of Lewis and Brønsted acidic sites in H-MFI and H-BEA zeolites: a thermodynamic and ab initio study. *Thermochim Acta.* 2004;418:3–9.
18. Desmartin-Chomel A, Flores JL, Bourane A, Clacens JM, Figueras F, Delahay G, et al. Calorimetric and FTIR study of the acid properties of sulfated titanias. *J Phys Chem B.* 2006;110:858–63.
19. Auroux A, Gervasini A. Microcalorimetric study of the acidity and basicity of metal oxide surfaces. *J Phys Chem.* 1990;94:6371–9.
20. Solinas V, Ferrino I. Microcalorimetric characterisation of acid-basic catalysts. *Catal Today.* 1998;41:179–89.
21. Vartuli JC, Santiesteban JG, Traverso P, Cardona-Martinez N, Chang CD, Stevenson SA. Characterization of the acid properties of tungsten/zirconia catalysts using adsorption microcalorimetry and n-pentane isomerization activity. *J Catal.* 1999;187:131–8.