

WO₃/ZrO₂: a potential catalyst for the acetylation of anisole

R. Sakhivel¹, H. Prescott, E. Kemnitz*

Institut für Chemie, Humboldt-Universität zu Berlin, Brook Taylor Str. 2, 12489 Berlin, Germany

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Abstract

WO₃/ZrO₂ catalysts were prepared by coprecipitation with 5, 10, 15, 19, and 25 wt.% WO₃. These catalysts were characterized by XRD, BET, FTIR photoacoustic spectroscopy (pyridine adsorption), and NH₃-TPD, and tested for the acetylation of anisole with acetic anhydride. The catalytic yields of 2- and 4-methoxyacetophenone are found to be proportional to the ratio of Brønsted to Lewis acid site band intensities with WO₃ loading up to 19 wt.%.

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1. Introduction

Growing environmental concerns has forced the scientific community to look for alternatives to the corrosive liquid acids, such as HF, H₂SO₄ and BF₃, used as catalysts. One possibility is the environmentally friendly solid acid, SO₄/ZrO₂. Sulfated zirconia (SZ) is a well-known solid acid catalyst, and it effectively catalyses a variety of isomerization reactions and the acylation of aromatics reactions [1–3]. Unfortunately, SZ undergoes deactivation due to sulphur loss during thermal treatment [4,5]. This has led to the development of a thermally stable tungstated zirconia (WZ). Although WZ is comparatively less active than SZ at lower temperatures (<100 °C) in alkane isomerization reactions, it is more stable at higher temperatures [6] and in a reducing atmosphere [5]. The modifying of zirconia with WO₃ similar to the sulfation of zirconia stabilizes the tetragonal ZrO₂ phase [7,8]. Although Fe and Mn promote the activity of SZ, they do not improve the activity of WZ in the *n*-pentane isomerization re-

action [9]. Acid sites in WZ are generated by the interaction of WO₃ and ZrO₂ during the crystallization of tetragonal ZrO₂ [10]. The acid strength and catalytic activity of WZ depend on the method of catalyst preparation. The impregnation of ammonium metatungstate is carried out on hydrous zirconia rather than the pre-calcined, anhydrous ZrO₂ with consequent calcination at higher temperatures. Aging of the hydrous zirconia under refluxing prior to impregnation of the tungsten oxide precursor and calcination resulted in higher activities [7]. Catalyst preparation with coprecipitation of the oxides of tungsten and zirconium yielded a catalyst with much stronger acid sites [11] (compared to catalysts prepared by impregnation). Although WZ has been used as a catalyst in the acetylation and benzylation of toluene on WZ [12], details such as the optimum concentration of WO₃ and reaction temperature are not given. The present study focuses on the acetylation of anisole on WZ prepared with various concentrations of WO₃ by coprecipitation followed by aging under reflux and calcination. The catalytic activities, acid strengths, and physical surface properties of the WO₃/ZrO₂ samples are discussed here. A WZ sample prepared by impregnation is also briefly presented, which was not fully characterized. This sample was exclusively tested for the acetylation of anisole to compare catalytic results of coprecipitated and impregnated WZ.

* Corresponding author. Tel.: +49 30 2093 7555; fax: +49 30 2093 7277.
E-mail address: erhard.kemnitz@chemie.hu-berlin.de (E. Kemnitz).

¹ On leave from Regional Research Laboratory, Bhubaneswar 751013, Orissa, India.

2. Experimental

The WO₃/ZrO₂ samples of WO₃ on ZrO₂ were prepared by homogeneous hydroxide coprecipitation with WO₃ concentrations of 5, 10, 15, 19, and 25 wt.%. Ammonia (12.5% aqueous solution) was added dropwise to a mixed aqueous solution of ZrOCl₂·8H₂O (Fluka, ≥99%) and ammonium metatungstate (Fluka) under stirring until pH 9. The coprecipitate was washed with NH₄OH solution (pH 9) and aged under refluxing at 100 °C for 24 h. It was then filtered, oven dried at 110 °C overnight, ground, and calcined at 700 °C for 3 h in air.

The impregnated catalyst, imp-WO₃/ZrO₂ (20 wt.% of WO₃), was prepared by hydroxide precipitation of an aqueous solution of ZrOCl₂·8H₂O (Fluka, ≥ 99%) by dropwise addition of NH₃ (12.5% aqueous) under stirring till pH 9. The precipitate was washed, oven dried (110 °C), and then impregnated with ammonium metatungstate. After impregnation, the sample was oven dried again and calcined at 500 °C for 3 h.

The X-ray powder diffraction patterns of all the samples were collected on an X-ray diffractometer, RD7 (Rich, Seifert & Co., Freiberg) using Cu Kα radiation (Ni-filter, 2θ = 5–64°, 0.050 step, 5 s/step). The mean pore volume, pore diameter, and specific surface area were determined from nitrogen adsorption isothermal experiments at 77 K by the BJH and BET methods, respectively, with help of an automated ASAP 2000 Micromeritics Instrument.

Semiquantitative determination of both Lewis (L) and Brønsted (B) acid sites of the catalysts were carried out at room temperature (RT) by FTIR photoacoustic spectroscopy (FTIR system 2000, Perkin Elmer spectrometer) using an MTEC cell. The powdered sample (~250 mg) was pretreated at 150 °C for 30 min under flowing Ar. Half of the sample was taken out of the reactor and measured at RT (as a blank) from 4000 to 400 cm⁻¹. The remaining sample in the reactor was treated with 30 μl of pyridine twice in an interval of 5 min at 150 °C and flushed with flowing Ar for 15 min to remove the physisorbed pyridine. The spectrum of the pyridine adsorbate complexes was measured as described above. Bands at about 1540 cm⁻¹ (B), 1491 cm⁻¹ (B + L), and 1445 cm⁻¹ (L) indicate Brønsted and Lewis acid sites. The spectra were normalised according to [3] and one-third of the intensity

of the Lewis acid site band observed at 1445 cm⁻¹ (L) was deducted from the intensity of the band found at 1491 cm⁻¹ (B + L) to get the intensity of that band, which can be exclusively attributed to Brønsted acid sites; the corrected intensities of the 1491 cm⁻¹ bands are given in Table 1. FTIR photoacoustic spectra of the pyridine adsorbate complexes of 10-WO₃/ZrO₂ and 19-WO₃/ZrO₂ were also measured at desorption temperatures of 250 and 450 °C. This involved (a) heating the sample at 10 °C/min after pyridine adsorption at 150–250 or 450 °C, (b) holding the temperature for 10 min, and (c) measuring the spectra thereafter at room temperature.

The acid site concentration and distribution of the catalysts were determined quantitatively by temperature programmed desorption of ammonia (NH₃-TPD). The granular sample (~0.5 mm, 200 mg) was pretreated at 500 °C in a quartz reactor for 1 h in flowing Ar, cooled down to 120 °C, treated with a stream of Ar and NH₃, flushed with Ar until physisorbed NH₃ was completely removed, and cooled down to 80 °C. The NH₃-TPD temperature program was carried out from 80 to 500 °C (10 °C/min) holding 500 °C for 30 min; the intensity of NH₃ band at 930 cm⁻¹ was monitored with FTIR spectroscopy throughout the measurement. The desorbed NH₃ was collected in an excess amount H₂SO₄ and its amount was determined by back titration with NaOH.

Acetylation of anisole was carried out with acetic anhydride. The catalyst (~300 mg) was added to a mixture of anisole (10.8 g, 90 mmol, Fluka, ≥99%) and acetic anhydride (1.02 g, 10 mmol, Fluka, ≥99%) in a mole ratio of 10:1, *n*-dodecane (0.05 g, 0.3 mmol, Fluka, 95%, GC internal standard). A reaction temperature of 50 °C was maintained for 3 h. Reaction temperatures of 50, 80, 100, 150 °C were studied using the catalyst, 19-WO₃/ZrO₂. Then, the catalyst was separated. The reaction mixture was analysed gas chromatographically before and after the reaction using a Varian 3400 GC (Restec Corp., USA) with a wide bore column DB 5 (length 15 m, inner diameter 0.53 mm), FID: 300 °C, injector: 280 °C, temperature program: 90 °C (1 min) to 180 °C (20 °C/min), 0.3 μl sample. The main products are 2- and 4-methoxyacetophenone with a ratio of 1:99 and acetic acid. The conversion of acetic anhydride and yield of methoxyacetophenones are given in Table 1.

Table 1
Physico-chemical characterization and catalytic activities of various catalysts

Catalyst	S _{BET} (m ² /g)	V _P (cm ³ /g)	D _P (Å)	FTIR photoacoustic relative band intensities			NH ₃ -TPD acid site concentration (mmol/g)	Acetylation at 50 °C (3 h)	
				B (1540 cm ⁻¹)	B (1491 cm ⁻¹)	L (1445 cm ⁻¹)		Conversion (%)	Yield (%)
5-WO ₃ /ZrO ₂	103	0.28	110	1.5	5.0	7.0	n.d.	11	0
10-WO ₃ /ZrO ₂	87	0.22	102	3.2	6.7	6.7	0.208	35	24
15-WO ₃ /ZrO ₂	90	0.17	74	7.8	12.7	7.2	0.178	44	37
19-WO ₃ /ZrO ₂	97	0.14	60	9.5	15.3	4.1	0.208	49	38
25-WO ₃ /ZrO ₂	78	0.11	56	11.3	11.4	7.3	0.160	41	31

n.d.: not determined; B: Brønsted acid site; L: Lewis acid site.

3. Results and discussion

3.1. Phase characterization and surface properties

Fig. 1 shows the X-ray powder diffraction patterns of WO_3/ZrO_2 with WO_3 concentrations of 5, 10, 15, 19, and 25 wt.%. It reveals the formation of a single, tetragonal phase of ZrO_2 (PDF-No.: 42–1164) up to 19 wt.% WO_3 , whereas the WO_3/ZrO_2 sample with 25 wt.% WO_3 shows two separate phases, tetragonal ZrO_2 and monoclinic WO_3 (PDF-No. 43–1035). Thus, the maximum solid solubility of WO_3 in ZrO_2 is 19 wt. %.

The BET specific surface areas are given in Table 1. The sample with 5 wt.% WO_3 has a maximum surface area of $103 \text{ m}^2/\text{g}$, whereas the samples loaded with 10, 15, 19 and 25 wt.% have lower surface areas of 87, 90, 97, and $78 \text{ m}^2/\text{g}$, respectively. The pore volumes and pore diameters decrease with higher WO_3 concentrations from 5 to 25 wt. %.

3.2. Catalytic activity

The catalytic activities of WO_3/ZrO_2 samples found for the acetylation of anisole with acetic anhydride are given in Fig. 2 and Tables 1 and 2. Both the conversion and the yield of 2- and 4-methoxyacetophenone at 50°C increase with the addition of WO_3 up to 19 wt.%; maximum activity is observed for 19 wt.% WO_3 with a catalytic yield of 38%. On the other hand, the impregnated sample, imp- WO_3/ZrO_2 with 20 wt.% WO_3 , was catalytically inactive. The catalytic activity of the coprecipitated sample decreases with a higher amount of WO_3 (25 wt.%) (catalytic yield: 31%). This could be due to surface acid site blockage by the separate WO_3 phase. The catalytic activity of 19- WO_3/ZrO_2 improves at

higher reaction temperatures. At 80°C , 74% of acetic anhydride was converted with 63% yield of the methoxyacetophenones. The highest catalytic activity of 19- WO_3/ZrO_2 was achieved, when the reaction was carried out at 100°C : 89% conversion, 92% selectivity, and 82% yield (Table 2). A higher reaction temperature of 150°C led to a slight decrease in conversion (89 \rightarrow 73%) and a drastic decrease in selectivity (92 \rightarrow 67%) and yield (82 \rightarrow 49%), which cannot be explained at this time.

3.3. Correlation between the catalytic activity and acidic properties

The acid site concentration and distribution of samples are given in Table 1 and Fig. 3, respectively. The 10, 15, 19, and 25 wt.% of WO_3/ZrO_2 samples have acid site concentrations of 0.208, 0.178, 0.208, and 0.160 mmol/g, respectively. The catalysts, 10- WO_3/ZrO_2 and 19- WO_3/ZrO_2 , have an identical acid site concentration of 0.208 mmol/g, which is the highest observed, but 19- WO_3/ZrO_2 exhibits a higher catalytic activity than 10- WO_3/ZrO_2 . The sample, 15- WO_3/ZrO_2 , has a slightly higher acid concentration than 25- WO_3/ZrO_2 (0.178 and 0.160 mmol/g, respectively). This correlates with the catalytic activity: higher acid site concentrations yield higher catalytic activities. The area of the NH_3 profile in the temperature regions, < 250 , 250–450, and $> 450^\circ\text{C}$, are defined here, respectively, as “weak”, “medium”, and “strong” acid sites to understand the distribution of acid site concentration. Similar distributions of weak and medium acid sites are observed for 10, 15, and 19 wt.% WO_3 loaded catalysts, whereas 25- WO_3/ZrO_2 has slightly higher concentrations of both. The distribution of “strong” acid sites decreases with increasing incorporation of WO_3 from 10 to 25 wt.%. This does not

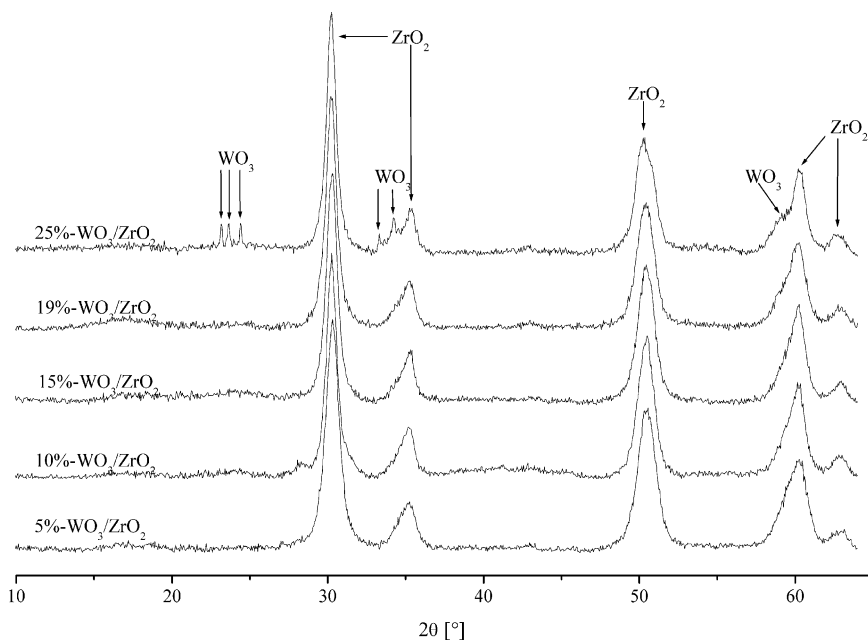


Fig. 1. X-ray powder diffractograms of the WO_3/ZrO_2 catalysts.

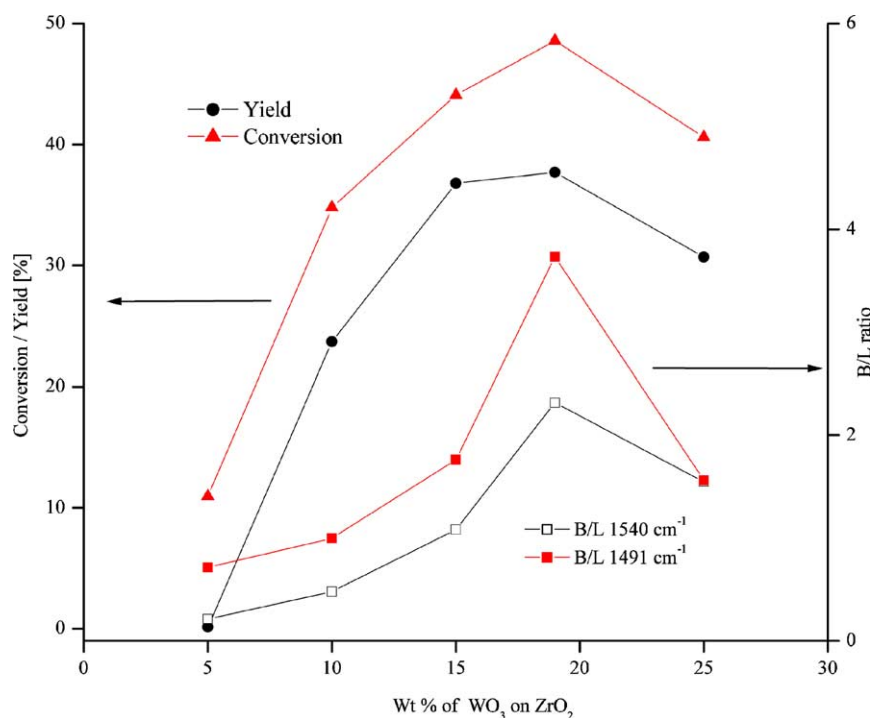


Fig. 2. Correlation of B/L ratio with catalytic activity.

Table 2

Catalytic activity of 19-WO₃/ZrO₂ at different reaction temperatures for the acetylation of anisole

Reaction temperature (°C)	Conversion (%)	Yield (%)
50	49	38
80	74	63
100	89	82
150	73	49

directly correlate with the catalytic activity and B/L ratios and indicates that factors other than the strength of the acid sites may influence the experimental data, which has been commented on before [13,14]. The sample, 25-WO₃/ZrO₂, has a lower concentration of strong acid sites than 19-WO₃/ZrO₂. The decrease in catalytic activity for this sample, however, is probably due to surface Brønsted acid site blockage by the WO₃ phase [15].

The relative intensity of bands observed in the FTIR photoacoustic spectra of pyridine adsorbate complexes on the catalysts is presented in Table 1. Both Brønsted and Lewis acid sites are present in all the samples and identified with the bands at 1540 cm⁻¹ (B), 1491 cm⁻¹ (B + L), and 1445 cm⁻¹ (L). The Brønsted acid site band (1491 cm⁻¹) intensity (obtained after removal of Lewis contribution) increases with WO₃ incorporation up to and at 19 wt.% and then decreases with 25 wt.% of WO₃. On the other hand, the intensity of Lewis acid site bands (1445 cm⁻¹) is similar for all the samples, except for 19-WO₃/ZrO₂. A lower amount of Lewis acid sites and a higher number of Brønsted acid sites are observed for 19-WO₃/ZrO₂ in comparison to the other samples,

for example 10-WO₃/ZrO₂ (compare Fig. 4a and d). Further, the band intensity ratio of Brønsted to Lewis (B/L) acid site (Fig. 2) increases gradually from 5 to 19 wt.% WO₃ and goes through a maximum with 19 wt.% WO₃. The ratio then decreases with 25 wt.% WO₃. The decrease in B/L ratio above 19 wt.% could be due to the blocking of Brønsted acid sites by the WO₃ phase observed by XRD. Thus, a maximum amount of Brønsted acid sites is obtained with 19 wt.% WO₃.

The trend in B/L ratio and Brønsted acid site band intensity (at 1491 cm⁻¹) both directly correlate with the catalytic activity in the acetylation of anisole. A similar correlation is not found for the Lewis acid site band intensity. The catalytic activity in the acetylation of anisole reaction is dependent on Brønsted acid sites, which supports the conclusion drawn by Quaschnig et al. [3] for the benzylation of anisole. Therefore, the maximum activity observed for 19-WO₃/ZrO₂ is due to the maximum number of Brønsted acid sites generated by the higher interaction of WO₃ with ZrO₂.

Fig. 4 shows the FTIR photoacoustic spectra of pyridine adsorbate complexes on 10-WO₃/ZrO₂ and 19-WO₃/ZrO₂ at 150 °C (Fig. 4a and d) and desorbed at 250 (Fig. 4b and e), and 450 °C (Fig. 4c and f). In both cases, the intensity of Lewis acid site band (1445 cm⁻¹) decreases with an increase in desorption temperature. The broad Brønsted acid site band (1540 cm⁻¹ in Fig. 4a and c) decreases in area and becomes sharper with increasing temperature, 150–450 °C. Although the intensity of the 1491 cm⁻¹ (Brønsted and Lewis acid sites band) band remains relatively unchanged at desorption temperatures of 150 and 250 °C, a considerable decrease in intensity is observed for both samples after pyridine desorption at

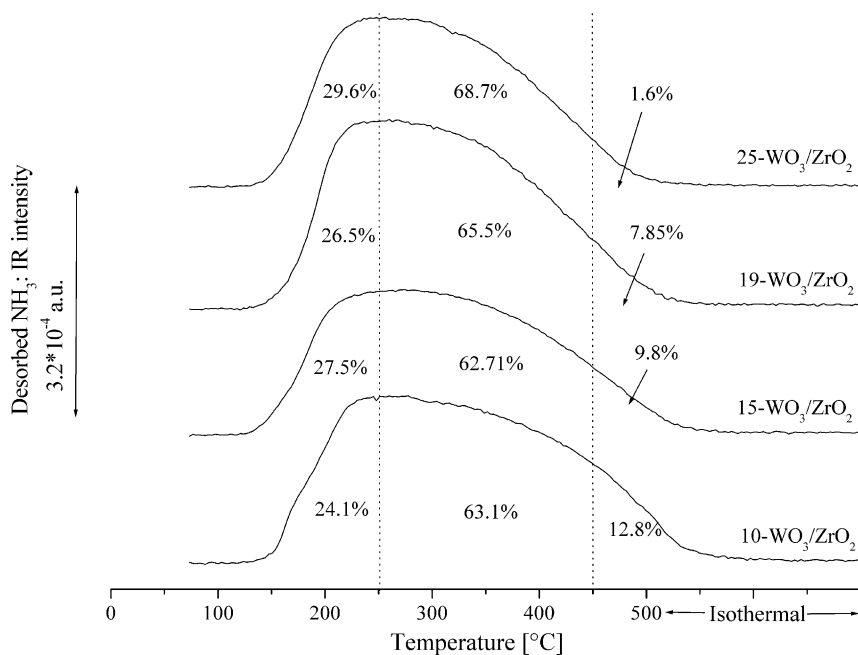


Fig. 3. NH_3 -TPD profiles of the indicated catalysts.

450 °C. The B/L ratio of these spectra increases with a higher desorption temperature (from 150 to 450 °C), and the B/L ratio of 19- WO_3/ZrO_2 is higher than that of 10- WO_3/ZrO_2 at all three temperatures, 150, 250, and 450 °C. The catalyst, 10- WO_3/ZrO_2 , with a higher concentration of “strong” acid sites (>450 °C) in NH_3 -TPD does have some Lewis acid sites (band at 1445 cm^{-1}) after desorption of pyridine at 450 °C,

whereas the band at 1445 cm^{-1} of the 19- WO_3/ZrO_2 , which has a lower concentration of “strong” acid sites, disappears completely after pyridine desorption at 450 °C. The “strong” acid sites observed in the NH_3 -TPD of 10- WO_3/ZrO_2 (Fig. 3) could be attributed to the Lewis acid sites still present at 450 °C (Fig. 4) with the assumption that both NH_3 and pyridine chemisorb at the Lewis acid site with same strength.

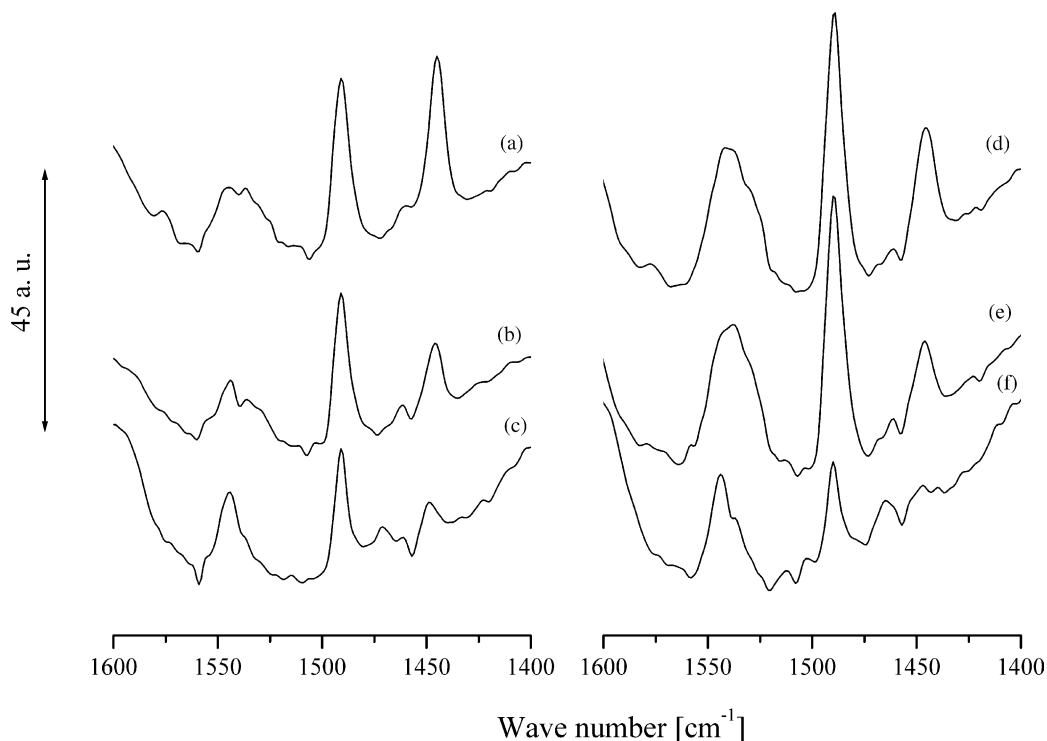


Fig. 4. FTIR photoacoustic spectra of the pyridine adsorbate complexes of 10- WO_3/ZrO_2 : (a) after pyridine adsorption at 150 °C and desorption temperatures of (b) 250 °C and (c) 450 °C and of 19- WO_3/ZrO_2 (d) after pyridine adsorption at 150 °C and desorption temperatures of (e) 250 °C and (f) 450 °C.

The impregnated catalyst, WO_3/ZrO_2 with 15 wt.% W, reported in [12], achieved only 3% yield in the acetylation of toluene. The coprecipitated catalyst, 19- WO_3/ZrO_2 (15 wt.% W or 19 wt.% WO_3) reported in this study achieved 82% yield in the acetylation of anisole at the same reaction temperature (100°C) after 3 h. A drastic improvement in catalytic activity, 38% versus 0% yield, is observed when comparing 19- WO_3/ZrO_2 (calcination at 700°C) with imp- WO_3/ZrO_2 at 50°C (calcination at 500°C). This is a direct result of the much more effective method of preparation, coprecipitation, and the higher calcination temperature.

4. Conclusions

- a. The WO_3/ZrO_2 catalysts have both Brønsted and Lewis acid sites.
- b. The strong acid sites detected by NH_3 -TPD above 450°C do not enhance catalytic activity in the acetylation reaction.
- c. The maximum Brønsted acidity and catalytic activity is achieved with the WO_3 loading of 19 wt.%.
- d. Highest conversion and yields are obtained with a reaction temperature of 100°C .
- e. Coprecipitation and high calcination temperatures lead to catalytically very active WZ phases.
- f. A higher loading of WO_3 (25 wt.%) on ZrO_2 leads to surface acid site blockage.

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