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Higher Brønsted acidity of WO_x/ZrO_2 catalysts prepared using a high-surface-area zirconium oxyhydroxide

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ABSTRACT

The precipitated zirconium oxyhydroxide, ZrOH(H), was used as a support for tungstate loading, where its specific surface area was 1.5-fold higher than that of the analogous sample obtained commercially, ZrOH(L). Due to this difference, crystalline WO_3 and ZrO_2 (tetragonal and monoclinic) were formed at a higher calcination temperature by 150 K for WZrOH(H) than for WZrOH(L) when tungstate was loaded. For WO_x/ZrO_2 with different W surface densities produced by calcination at 723–1173 K, pyridine-IR experiment and Raman spectroscopy revealed that more Brønsted acid sites were present for WZrOH(H) calcined at 1023 and 1073 K than for WZrOH(L) calcined at 873 K while distorted Zr-stabilized WO_3 nanoparticles were found for these samples. Thus, the former samples showed the superior activity to the latter in the dehydration of formic acid. The linear relationship between the catalytic performance and Brønsted acidity was observed, explaining that WO_x/ZrO_2 with more Brønsted acid sites is more active in the dehydration reaction. Consequently, the enhanced Brønsted acidity and catalytic activity of WZrOH(H) resulted from the use of zirconium oxyhydroxide with a high surface area for tungstate loading.

1. Introduction

Tungstated zirconia (WO_x/ZrO_2), developed first by Hino and Arata [1], has been considered to be an important solid acid catalyst due to superior properties such as thermal stability, strong acidity, and strong resistance upon exposure to H_2, O_2 and H_2O. Particularly, WO_x/ZrO_2 is active at low temperatures in the isomerization of C_4–C_8 alkanes [2–5]; for instance, it showed better catalytic performance than zeolite β in the isomerization of *n*-pentane [6]. The superior activity of WO_x/ZrO_2 has been examined in other acid-catalyzed reactions including Mannich reaction [7], acylation [8], alkylation [9,10] and dimerization [11]. Besides, metal-promoted WO_x/ZrO_2 catalysts (metal: Pt, Pd, Au, Fe, etc.) has been studied in multi-step reactions requiring both metal and acid functions [12].

The acidity and catalytic performance of WO_x/ZrO_2 largely depends on W surface density varying with the activation temperature, the W loading and the nature of the starting Zr support. Boyse and Ko revealed three types of WO_x clusters, such as mono-tungstate, poly-tungstate and crystalline WO_3, of which each type is controlled by the activation temperature [13]. In terms of the tungstate loading, Scheithauer et al. found that the presence of WO_x stabilized the tetragonal ZrO_2 phase and increased the intrinsic BET surface area, and that a relatively dense overlayer containing W–O–W linkages and terminal W=O groups formed a three-dimensional network of interconnected WO_6 octahedra near the theoretical monolayer coverage [14]. Soultanidis et al. related the *n*-pentane isomerization activity to the Zr support nature and the W surface density [15]. They claimed that amorphous zirconium oxyhydroxide ($ZrO_x(OH)_{4-2x}$) was a better support than crystalline zirconia (ZrO_2) and the best activity was obtained at 5–6 W surface density ($\rho_{w,surf}$; W atoms nm^{-2}) using $ZrO_x(OH)_{4-2x}$ as a support. In their another work [16], $ZrO_x(OH)_{4-2x}$-supported WO_x was more active than ZrO_2-supported WO_x in the dehydration of methanol to dimethyl ether and showed the best activity when the surface density was 6.2 W nm^{-2} (0.8–1 nm tungstate cluster). Ross-Medgaarden et al. described the formation of Zr-stabilized distorted WO_3 in nanoparticle sizes (NPs) in the monolayer region showing the best activity in methanol dehydration [17]. Distorted WO_3 NPs were characterized by Raman absorption bands in the range 820–850 cm^{-1} and 900–925 cm^{-1}. Meanwhile, it was pro-

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posed that the high acidity of WO_x/ZrO_2 originates from a conjugate Brønsted-Lewis site [18].

From these previous reports, it can be speculated that when $ZrO_x(OH)_{4-2x}$ with a higher surface area is used, the final WO_x/ZrO_2 catalyst shows a larger amount of Brønsted/Lewis acid sites and thereby an improved activity in acid-catalyzed reactions. Thus, we herein have prepared $ZrO_x(OH)_{4-2x}$ with a high surface area based on our recent work [19]. After the tungsten precursor was loaded into the resulting material by impregnation, the activation was conducted at different temperatures in order to vary the W surface density over WO_x/ZrO_2 catalysts. The prepared materials, $ZrO_x(OH)_{4-2x}$ and WO_x/ZrO_2, were characterized by N_2 physisorption, thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC), powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS). In addition, the acid characteristics of WO_x/ZrO_2 catalysts were obtained by NH_3-temperature programmed desorption (NH_3-TPD) and pyridine-chemisorbed infrared spectroscopy (pyridine-IR). For the activity test, the decomposition of formic acid (HCOOH) was conducted because it is well known that acid catalysts exclusively promote the dehydration reaction ($HCOOH \rightarrow H_2O + CO$), but not the dehydrogenation reaction ($HCOOH \rightarrow H_2 + CO_2$) mainly taking place over metal catalysts [20]. Finally, the measured activities of WO_x/ZrO_2 catalysts were correlated with their densities of Brønsted acid sites.

2. Experimental

2.1. Preparation of amorphous zirconium oxyhydroxide

$ZrO_x(OH)_{4-2x}$ with a high surface area, labelled as ZrOH(H), was prepared by precipitation. An aqueous ammonia solution (28 wt.% NH_4OH, SK Chemical) was added dropwise into 0.5 M aqueous zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, Kanto Chemicals, 99%) at room temperature until the solution pH reached 9.2. Then, the mixed solution was refluxed at 373 K for 72 h, which is called "digestion". The so-obtained filter cake was washed several times to eliminate chloride ions and dried at room temperature for 1 day. For comparison, commercial $ZrO_x(OH)_{4-2x}$ (purity 97%), labelled as ZrOH(L), was purchased from Sigma Aldrich.

2.2. Synthesis of tungstated zirconia catalysts

WO_x/ZrO_2 catalysts were synthesized by incipient wetness impregnation of an aqueous solution of ammonium metatungstate hydrate ($(NH)_4H_2W_{12}O_4 \cdot xH_2O$, Sigma Aldrich, 99.99%) onto the prepared ZrOH(H) and commercial ZrOH(L), where the W content was 15 wt% in all samples. After drying at 378 K overnight, crushing and sieving to less than 200 μm, the W-loaded ZrOH(H) sample was calcined at a certain temperature for 4 h in an air flow of 100 ml min^{-1} with a ramping rate 10 K min^{-1}. The resulting tungstated zirconia was named as WZrOH(H)-*x*, where *x* represents the calcination temperature of 723, 873, 1023, 1073 or 1173 K. ZrOH(L) support was also used for W loading and the resulting catalyst was named as WZrOH(L)-*x* with *x* of 723, 873, 1023 or 1173 indicating the calcination temperature in a unit of Kelvin.

2.3. Characterization of the prepared samples

PXRD patterns were acquired on a Rigaku SmartLab diffractometer using a Cu Kα radiation source (λ = 0.154056 nm, 45 kV and 200 mA). PXRD patterns were collected in the 2θ range 10–80° with a step increment of 0.02°. Micromeritics 3Flex instrument was used for measuring the Brunauer-Emmett-Teller (BET) surface area at 77 K after degassing of the sample (0.2 g) at 298 K for $ZrO_x(OH)_{4-2x}$ or 373 K for WO_x/ZrO_2 under vacuum for 1 h. TGA-DSC measurement was conducted using a SDT Q600 (TA Instruments). The sample (*ca.* 10 mg) was loaded on alumina pan and the temperature was raised from room temperature to 1273 K with a heating rate 10 K min^{-1} in a nitrogen gas flow 100 ml min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantrea II (Ulvac-PHI) with a monochromatic Al K_α radiation. All spectra were calibrated using a standard C 1 s binding energy of 248.6 eV as reference.

Field emission scanning electron microscopy (FE-SEM) images were taken in a FEI Nova NanoSEM 450 microscope with an electron dispersive X-ray spectrometer (EDS) operated in the range 10–15 kV after the samples were coated by Pt. For high-resolution transmission electron microscopy (HRTEM) coupled with electron diffraction, a JEM 2100F microscope (JEOL) was used with a Gatan DigitalMicrograph imaging filter. Raman spectrometer (NRS-3100, JASCO) was used with 532 nm laser excitation generated by a SOC green laser (output power = 50 mW, sample power = 2.3 mW). Raman spectra were obtained in the range 200–1200 cm^{-1} with 1 cm^{-1} resolution after vacuum drying of the sample disk at 368 K for 1 day to prepare a dehydrated sample.

NH_3-TPD experiment was conducted in an AutoChem 2910 (Micromeritics). Prior to the analysis, the sample was pretreated in a He flow of 30 ml min^{-1} at 523 K for 2.5 h. The sample was cooled to 373 K and then exposed to 5% NH_3/He flow of 30 ml min^{-1} for 30 min. After acquiring a stable TCD baseline, the sample was heated to 1073 K at a rate of 10 K min^{-1}, where the emitted gases were analyzed by a quantitative gas analyzer (Hiden Analytical). For pyridine-IR analysis, a Thermo Nicolet 6700 equipped with a MCT-A detector (Thermo Scientific) was used, where the spectrum was obtained with 32 scans at a resolution 4 cm^{-1}. The sample disk (50 mg) was loaded inside a Specac HTHP cell and pretreated at 523 K for 1.5 h under vacuum. After pretreatment, the sample was cooled to 423 K and exposed to 0.5 μl pyridine at 423 K for 30 min.

2.4. Activity test

The activity test was conducted in a quartz reactor into which the catalyst of 25 mg was loaded. After pretreatment at 673 K in a He flow and cooling to either 383 K (at this temperature the conversion of HCOOH is below 5% in every runs) or 473 K, an isothermal activity was obtained at a formic acid partial pressure of 5.7 kPa. The feed stream was acquired by flowing 1% N_2/He (100 ml min^{-1}) into a Pyrex saturator containing formic acid (Sigma Aldrich) maintained at 298 K for all runs. The product stream was connected to an *on-line* gas chromatograph (Agilent 7890B) equipped with a packed column (Porapak Q 80/100, 12 ft × 1/8 in × 2.1 mm) and a thermal conductivity detector. In order to prevent condensation of formic acid vapors, all stainless steel lines of 1/8 in. diameter were heated at 363–393 K. The conversion of formic acid was calculated by the difference between the inlet and outlet molar flowrates of formic acid. Note that the selectivity to CO was 100% (i.e., no CO_2 formation) for all tungstated zirconia catalysts used in this work.

3. Results and discussion

3.1. Physicochemical properties of ZrOH(H) vs. ZrOH(L)

The precipitated $ZrO_x(OH)_{4-2x}$ sample prepared in this work and the commercial $ZrO_x(OH)_{4-2x}$ sample were characterized prior to tungstate loading. PXRD analysis revealed that ZrOH(L) and ZrOH(H) samples are all X-ray amorphous (Fig. S1). When we measured their BET specific surface areas and pore volumes by N_2 physisorption at 77 K, ZrOH(H) showed higher textural properties than ZrOH(L): 414 vs. 280 $m^2\,g^{-1}$ for the BET surface area and 0.56