Effect of Nb doping in WO$_3$/ZrO$_2$ catalysts on gas phase dehydration of glycerol to form acrolein†

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Gas-phase dehydration of glycerol to produce acrolein was investigated over tungstated zirconia catalysts with and without niobium doping, in order to correlate the catalytic activity and life-stability with the acid/base properties of the catalysts. The results of NH$_3$- and CO$_2$-TPD experiments showed that the tungstated zirconia catalysts contained both acidic and basic sites, and the amounts decreased with the increase in calcination temperature. The most suitable calcination temperature for 20% WO$_3$/ZrO$_2$ as the catalyst in the gas phase dehydration of glycerol to form acrolein was 450 ºC in consideration of achieving high acrolein yield and long lifetime of the catalyst. Not only the amount of acid but also the amount of base affected the acrolein yield. Doping a small amount of niobium further increased the life-stability of the catalysts, attributed to the decrease in the number of basic sites. The influence of Nb is mostly in neutralization of surface acidity electronically instead of geometric blocking of the basic sites. Moreover, fine tuning the ratio of acid/base sites was found to be important in achieving good catalytic performance in the gas-phase dehydration of glycerol to generate acrolein. The ratio of acid/base sites in the range of 4–5.4 gave the highest glycerol conversion, and acrolein yield and lowest catalyst decay rate. The spent catalysts were easily regenerated by calcination at 450 ºC, and the catalytic activities were retained well even after the second time of reuse.

Dehydration of glycerol to form acrolein has been exercised since 1930, Sherer-Kahlbaum claimed the first patent of acrolein production from glycerol in gas-phase over lithium phosphate supported on pumice stone. The rate of acrolein decomposition was found to be faster than that of acrolein formation in the absence of acid catalyst. Since then, sulfuric acid was used as the catalyst in liquid phase dehydration of glycerol. However, corrosion hazard and difficulties in handling and product separation are the drawbacks. Although solid acid catalysts such as clay and alumina supported phosphoric acid and heteropolyacids were effective as the dehydration catalysts in liquid phase, it is still hazardous to operate the reaction under supercritical water pressure.

Gas-phase dehydration of glycerol to produce acrolein has been promoted by solid acids. Dubois et al. studied the catalytic performances of various solid acids, including zeolites, NaFion and WO$_3$/ZrO$_2$, in gas-phase dehydration of glycerol, and concluded that solid acids with Hammett acities (HAs) in the range of −10 to −16 were suitable catalysts. They also reported for the first time that WO$_3$/ZrO$_2$ had high activity in catalyzing gas-phase dehydration of glycerol to produce acrolein. In 2007, Chai et al. examined a large group of solid materials including zeolites, SAPOs, metal oxides, supported phosphoric and heteropoly acids, and sulfated and tungstated zirconia, in catalyzing gas-phase dehydration of glycerol. They concluded that solids with HAs in the range of −3 to −8.2 were most active catalysts in generating acrolein. Among the solids, 15 wt% WO$_3$/ZrO$_2$ showed...
the highest glycerol conversion and acrolein selectivity. Nevertheless, deactivation of the catalysts with time-on-stream (TOS) was the main concerns. In 2011, Ulgen et al. reported the use of WO3/TiO2 instead of WO3/ZrO2 as the catalyst in gas-phase dehydration of glycerol, and they found that co-feeding of oxygen could reduce deactivation rate of the catalyst.

Niobium based catalysts have been tested in dehydration of glycerol to form acrolein. Chai et al. reported that the niobia calcined at 400 °C gave the highest glycerol conversion and acrolein selectivity. Shiju et al. studied silica supported niobia catalysts and found that the glycerol conversion and acrolein selectivity depended on the niobia loading and calcination temperature. However, in both aforementioned works, the niobia catalysts showed glycerol conversions decreased rapidly with TOS. Lauriol-Garbey et al. used zirconium and niobium mixed oxides (ZnNbO) as catalysts for glycerol dehydration. The ZnNbO catalysts gave the recorded high conversion of 82% even after 177 h on stream with acrolein selectivity remaining 72%. However, these results have not been repeated by other research groups. Lately, the same group reported SiO2-doped WO3/ZrO2 as catalysts in dehydration of glycerol. However, the catalytic lifetime was much shorter than that of ZrNbO. Recently, niobium species supported on a zirconium doped porous silica were used as the catalysts, but acrolein selectivity of 45 mol% was obtained after 2 h TOS. In the present study, we disclosed a novel finding that doping a small amount of niobium to WO3/ZrO2 catalysts would increase the life-stability of the catalysts. Moreover, relatively high acrolein selectivities (ca. 70%) could be retained. Efforts were put in correlation of the active sites with the decay rate of the catalysts.

2. Experimental methods

2.1 Catalyst synthesis

Tungstated zirconia was prepared by wet impregnation method. For the WO3/ZrO2 catalyst of 20% weight ratio, a solution containing 0.2636 g [NH4]2H2W12O40·xH2O dissolved in 5 mL deionized water was added dropwise onto 1.2926 g Zr(OH)4 powders under static condition, and the mixture was left steady for 1 h before the solvent was removed by rotary evaporation. After drying at 100 °C overnight, the powders were calcined in air at temperatures in the range of 400 to 800 °C for 3 h with a ramping rate of 1 °C min⁻¹. The niobium doped tungstated zirconia catalysts were prepared by the procedures similar to the foregoing method, except proper amounts of niobium oxalate were added in the solution of ammonium metatungstate hydrate for impregnation on Zr(OH)4 powders. After drying at 100 °C overnight, the powders were calcined at 450 °C for 3 h in air. The resultant materials were designated as X-NbWO3/ZrO2, where the WO3/ZrO2 weight ratios were kept at 20%, and X varied in 1, 3, and 5% is the Nb2O5/(WO3 + ZrO2) weight ratio.

2.2 Catalyst characterization

Powder X-ray diffraction (PXRD) patterns were recorded with a Panalytical X'Pert diffractometer using Cu Kα radiation in an operating mode of 45 kV and 40 mA. Nitrogen physisorption was carried out in a Micromeritics TriStar 3000 system. Prior to the physisorption, the sample was degassed at 200 °C under 10⁻² torr for at least 8 h. Acidity and basicity of the catalysts were determined by temperature-programmed desorption of NH3 and CO2, respectively, using an AutoChem 2910 system with a TCD detector. About 0.25 gram of the sample was heated in a 50 mL min⁻¹ of He flow at calcination temperature for 1 h to remove the adsorbed moisture. Then, 5% ammonia in He or pure CO2 gas (50 mL min⁻¹) was passed through the sample at 100 °C for 1 h, followed by purging the sample with pure He (30 mL min⁻¹) for another hour. The TCD signals of the effluent were recorded when the sample was heated from 100 to 600 °C with a ramping rate of 10 °C min⁻¹. FTIR spectra were conducted using a Nicolet Magna FT-IR 550 spectrometer. The resolution of the recorded spectra is 4 cm⁻¹. 25 mg of the sample was pressed into a disk and placed inside the cell. After heated at 450 °C under 10⁻⁴ torr for 1 h and cooled down to room temperature, the sample was exposed to pyridine vapor for 30 min and evacuated to 10⁻⁴ torr for another 30 min to remove pyridine vapor in the gas phase. The IR spectra were recorded under 10⁻⁴ torr while the temperature was raised to 400 °C at 100 °C intervals. Scanning electron microscopy (SEM) photographs were taken using a Hitachi S-4800 Field Emission Scanning Electron Microscope.

2.3 Catalytic reaction

Gas-phase dehydration of glycerol was carried out at 290 °C under ambient pressure in a vertical fixed-bed tubular quartz reactor. The catalyst (300 mg) in fine powders was mixed with quartz (300 mg) and then sandwiched in the middle of the reactor with quartz wool. Prior to the reaction, the catalyst was pretreated at 290 °C for 1 h under flowing dry nitrogen (60 mL min⁻¹). An aqueous solution of 10 wt% glycerol was fed into the reactor by a syringe pump with a flow rate of 8 mL h⁻¹. The products were collected hourly by an ice-water trap and analyzed by a gas-chromatography (GC) equipped with a capillary column (BP-20) and a FID detector. The glycerol conversion and selectivities of identified products were calculated according to the following equations:

\[ \text{Conversion} (%) = \frac{\text{initial mol} - \text{final mol}}{\text{initial mol of glycerol}} \times 100\% \]  

\[ \text{Selectivity} (%) = \frac{\text{specific product in mol}}{\text{initial mol} - \text{final mol}} \times 100\% \]

3. Results and discussion

3.1 Effect of calcination on WO3/ZrO2 catalysts

3.1.1 Characterization. XRD patterns of the WO3/ZrO2 catalysts show that calcined at 400 °C to be amorphous (Fig. 1). As the calcination temperature increases, the peaks of the tetragonal ZrO2 (2θ = 30.3, 34.4, 50.3 and 60.0°) start to show and grow with temperature. At calcination temperature of 800 °C, monoclinic ZrO2 (characteristic peaks at 2θ = 28.2 and 31.5°) appears. Meanwhile, the monoclinic WO3 phase (2θ = 31.1°) is observed.
temperatures. A decrease in surface area and increase in pore diameter are observed with increasing the calcination temperature, and both are originated from sintering of the metal oxide particles at high temperatures.

The derived textural properties are given in Table 1.

Table 1 Textural properties of WO3/ZrO2 catalysts calcined at different temperatures and those doped with Nb

| Sample           | \(S_BET\) (m² g⁻¹) | Pore diameter (nm) | Pore volume (cm³ g⁻¹) |
|------------------|---------------------|--------------------|-----------------------|
| WO3/ZrO2-400     | 254                 | 3.7                | 0.241                 |
| WO3/ZrO2-450     | 223                 | 4.4                | 0.222                 |
| WO3/ZrO2-500     | 189                 | 5.1                | 0.248                 |
| WO3/ZrO2-600     | 138                 | 5.3                | 0.221                 |
| WO3/ZrO2-700     | 134                 | 6.3                | 0.239                 |
| WO3/ZrO2-800     | 62                  | 12                 | 0.224                 |
| 1% NbWO3/ZrO2-450| 233                 | 5.0                | 0.278                 |
| 3% NbWO3/ZrO2-450| 236                 | 5.3                | 0.302                 |
| 5% NbWO3/ZrO2-450| 242                 | 5.6                | 0.302                 |

* Determined by BJH method at peak maximum of pore size distribution profile.

23.2, 23.6 and 24.4° is also detected, suggesting that the crystalline WO3 is formed and dispersed on the ZrO2 support.

Nitrogen sorption isotherms of the calcined WO3/ZrO2 catalysts show type IV isotherms with the hysteresis loops appeared at \(p/p_0\) of 0.5–0.9, implying that these materials own mesopores. The derived textural properties are given in Table 1. A decrease in surface area and increase in pore diameter are observed with increasing the calcination temperature, and both are originated from sintering of the metal oxide particles at high temperatures.

NH3- and CO2-TPD experiments were used to measure the surface concentrations of acidic and basic sites, respectively. Fig. S1(A) (ESI†) shows that the total acid amounts of the WO3/ZrO2 catalysts measured by NH3-TPD decrease with calcination temperature, and the desorption peaks appear mainly in the range of 150–500 °C. These results are in consistency with that reported by García-Sancho et al.19 that the acidic strengths of the WO3/ZrO2 catalysts were in the range of weak to moderate. However, it is noticed that the sample calcined at 400 °C have additional desorption peaks at temperatures above 400 °C. The high temperature peak decreases in intensity and shifts to temperatures above 470 °C for the sample calcined at 450 °C.

Fig. S1(B) (ESI†) compares the base amounts of WO3/ZrO2 catalysts calcined at different temperatures measured by CO2-TPD experiment. Again, the total base amounts of the WO3/ZrO2 catalysts decrease with the calcination temperature. Three peak maxima can be seen at ca. 190, 380 and 530 °C on the sample calcined at 400 °C. The last high temperature peak is hardly seen on the sample calcined at 450 °C. In combination of the CO2-TPD and NH3-TPD results, it can be concluded that most of the surface hydroxyl groups condensate in the temperature range of 400–450 °C. Moreover, the high temperature peak observed on the NH3-TPD profile of WO3/ZrO2 calcined at 450 °C should not be due to condensation of surface hydroxyl groups. Instead, it corresponds to some strong acidic sites present on the sample.

Table 2 summarizes the acid and base densities based on the desorption peak areas of NH3-TPD and CO2-TPD, respectively, of WO3/ZrO2 calcined at different temperatures. It is noticed that those calcined at 400–600 °C have acid densities in a close range of 0.145–0.165 sites per nm², while those calcined at 700 and 800 °C have slightly lower and higher acid density of 0.130 and 0.183 sites per nm², respectively. On the other hand, base densities decrease almost linearly with the increase of calcination temperature. As the surface area decreases with calcination temperature, Fig. 2 shows that the acid and base densities as a function of surface area varied in the reverse trend. Base density increases with surface area, while acid density decreases with surface area but merely in a narrow range. These results infer that the amount of basic sites increases more abruptly than that of acid sites with the increase of surface area, and the latter is almost linearly proportional to the surface area.

3.1.2 Catalytic performance of WO3/ZrO2 calcined at different temperatures. Fig. 3 shows the results of gas phase dehydration of glycerol catalyzed by WO3/ZrO2 calcined at different temperatures. The glycerol conversions are all nearly 100% at the beginning, and then they decay with time on stream. Moreover, the decay rate is faster for the catalyst calcined at higher temperatures (Fig. 3A). On the other hand, the acrolein selectivities vary in similar trends with time-on-stream over all WO3/ZrO2 catalysts calcined at different temperatures (Fig. 3B). The acrolein selectivities increase in the first two hours and become steady with time on stream. The low acrolein selectivities in the first hour may be due to that the system is not in dynamic stability. Other researchers also reported lower than 90% calculated carbon balance in the initial reaction time.4,19,26 The conversions and products distribution in 3–4 h and those in 11–12 h are tabulated in Table 3. Acrolein is the major product, while hydroxylacetone (HA), acetaldehyde (AD), and allyl alcohol (AA) are minor products. Moreover, there are ca. 20 mol% of carbon
imbalance, which are shown as "Unknowns". Since all the used catalysts turn black, it is assumed that the Unknowns are coke and polymeric materials.

Dalil’s group has confirmed the coke formation at initial stage of gas phase glycerol dehydration, and the amount of coke deposited on WO3/TiO2 catalysts was found to increase with TOS.\(^{27-29}\) Since the selectivities of Unknowns over our catalysts are quite steady as a function of TOS (3–4 h vs. 11–12 h in Table 3). It is also consistent with the finding by Dalil’s group.

In comparison of WO3/ZrO2 calcined at different temperatures, those calcined at 450–700 °C give relatively higher acrolein selectivities of 68–71% (Fig. 1 and Table 3). Moreover, acrolein selectivities retain almost unchanged with TOS for catalysts calcined at 450–600 °C. For the catalyst calcined at lowest temperature, WO3/ZrO2-400, which contains the largest amounts of both acidic and basic sites, is most stable on TOS. However, the acrolein selectivity is among the lowest. In contrast, WO3/ZrO2 calcined at highest temperatures, WO3/ZrO2-700 and -800, have very fast decay rates and larger amounts of coke formation. Judging by the stabilities of the catalysts and high acrolein selectivities, the most suitable calcination temperature for WO3/
ZrO2 catalyst is 450 °C. Therefore, the catalysts studied hereafter were calcined at 450 °C.

3.2 WO3/ZrO2 catalysts doping with niobium

3.2.1 Characterization. The WO3/ZrO2 catalysts doping with 1–5% Nb2O5 show similar XRD patterns and nitrogen sorption isotherms as those of WO3/ZrO2-450. However, the surface area, pore diameter, and pore volume of the Nb-doped catalysts increase slightly in comparison to those of pristine WO3/ZrO2-450 (Table 1). These results infer that the incorporation of Nb in WO3/ZrO2 probably helps the dispersion of WO3 on ZrO2.

Fig. S2 (ESI†) shows the SEM photographs of WO3/ZrO2-450 catalyst and those doped with 1% and 3% Nb2O5. All of them are aggregates of nanoparticles ca. 10 nm in diameter and hard to estimate the individual oxide particle size. It is apparent that the doping of 1–3 wt% Nb2O5 does not cause the drastic change in the morphology of WO3/ZrO2 oxides, and no particles of other morphologies can be seen. This result implies that Nb is probably distributed homogeneously in the oxides.

Fig. S3 (ESI†) shows the NH3- and CO2-TPD profiles of WO3/ZrO2-450 catalysts doped with different amounts of Nb2O5, in comparison with those of pristine WO3/ZrO2-450. Fig. S3(A) (ESI†) shows that all the samples have similar NH3 desorption profiles: a broad band covering from 100 to 450 °C and a weak peak appeared above 450 °C. The possibility that the high temperature peaks are due to the condensation of surface hydroxyl groups can be excluded because they do not show in the CO2-TPD profiles (Fig. S3(B), ESI†). Hence, the presence of the small high temperature peaks in NH3-TPD profiles implies that the materials contain a small amount of strong acidic sites, probably attributed to formation of Nb2O5 clusters. Nevertheless, the majority of the acidic sites is in the weak to medium strength region. The intensities of the low temperature peaks decrease when only 1 wt% Nb2O5 is doped, and contrarily increase when it is further increased to 3 and 5% (Fig. S3(A), ESI†). However, the positions of desorption maxima retain at almost the same temperature around 200 °C, implying no significant change in acid strength of the catalysts with niobium doping.

The CO2-TPD profiles in Fig. S3(B) (ESI†) show that the base amounts decrease markedly when as low as 1% Nb2O5 is doped on WO3/ZrO2-450. The decrease in base amount is attributed to that Nb would neutralize the basic sites present on the zirconia support. However, the change in base amounts is less significant as the doping amount of Nb is further increased. The phenomenon can be explained by that the influence of Nb is mostly in neutralization of surface acidity electronically instead of geometrically blocking the basic sites. Moreover, Fig. S3(B)† shows that the basic sites of strongest strength with the CO2 desorption peak appeared above 400 °C are suppressed completely, while those of weakest strength with the desorption peak appeared at 100–330 °C are partially suppressed and those around 380 °C are hardly affected by Nb-doping.

The acid and base densities estimated from the desorption peak areas of NH3-TPD and CO2-TPD of Nb-doped WO3/ZrO2-450 samples are also summarized in Table 2. The acid densities are almost unchanged (0.143–0.146 nm−2), except the one doped with 1% Nb2O5 has lower value of 0.130 nm−2, while the base density decreases from 0.0510 nm−2 to 0.0313–0.0363 nm−2 with Nb doping. Fig. 2B plots the acid/base densities on Nb-doped WO3/ZrO2-450 as a function of surface area. It clearly shows that the acid densities are constrained in a narrow range while the base densities decrease with the increase in surface areas.

The nature of the acidic sites was examined by taking the FT-IR spectra of the catalysts after pyridine adsorption. Fig. 4 compares the FT-IR spectra of WO3/ZrO2-450 and that doped with 3% Nb2O5. At the desorption temperature of 100 °C, both samples show a strong peak at 1445 cm−1 attributing to pyridine adsorbed on the Lewis acid sites and a weak peak at 1545 cm−1 attributing to pyridine adsorbed on the Bronsted acid sites. In addition, the peaks at 1575 and 1610 cm−1 correspond to pyridine adsorbed on the weak and strong Lewis acid sites, respectively. At the desorption temperature of 300 °C, the 1545 cm−1 peak disappears completely while the 1445 and 1610 cm−1 peaks still retain some intensity for both samples. These results imply that both Nb2O5-doped and undoped WO3/ZrO2-450 materials contain mainly the Lewis acidic sites, and the strength of Lewis acidic sites is stronger than that of Bronsted acid sites. Moreover, 3% Nb2O3/ZrO2-450 contains slightly larger amount of strong Lewis acidic sites than WO3/ZrO2-450, judging by the peak intensities of the FT-IR spectra taken at desorption temperatures of 200–300 °C.

3.2.2 Catalytic performance of Nb-doped WO3/ZrO2. Fig. 5 shows the results of the dehydration of glycerol catalyzed by Nb-
doped WO₃/ZrO₂-450, in comparison to that of pristine WO₃/ZrO₂-450. The decay in glycerol conversion upon TOS is markedly slowed down over the Nb-doped catalysts. Table 4 compares the conversions and product distributions in 3–4 h and those in 23–24 h. All the catalysts give nearly complete conversion in 3–4 h TOS, but that drastic decreases to 28% after 23–24 h TOS is seen over pristine WO₃/ZrO₂-450. In contrast, all the Nb-doped catalysts can retain relatively high conversions of 74–81% after 23–24 h TOS. The catalytic stabilities vary with the doping amounts of Nb₂O₅ in the order of 5% < 1% < 3%. Acrolein is the major product, and the acrolein selectivity is not changed with Nb-doping or TOS. It retains around 70% over all the catalysts. HA, AD, and AA are obtained as the minor products and their selectivities are not affected by Nb-doping, while the Unknowns decrease slightly with Nb-doping. The optimal catalytic performance was obtained over 3% NbWO₃/ZrO₂-450 with 81% glycerol conversion and 72% acrolein selectivity at 24 h TOS.

### 3.3 Reusability of catalyst

The reusability of 3% NbWO₃/ZrO₂-450 catalyst was examined. The spent catalyst after reaction at 290 °C for 24 h was regenerated by calcination at 450 °C for 3 h to burn the coke disposed on the surface of the catalyst. Fig. S4 (ESI†) showed the TG profile of the used 3% NbWO₃/ZrO₂-450 catalyst obtained in air. The coke deposition on the used catalyst is about 19 wt%. Moreover, the profile indicates that 17 wt% is burned away at temperature below 450 °C and only 2 wt% coke is still remained after calcination at 450 °C. Fig. S5 (ESI†) compares the catalytic performances of the fresh and regenerated 3% NbWO₃/ZrO₂-450 catalysts. The results showed that the glycerol conversion and selectivity to acrolein are well retained even the catalyst is regenerated and reused for second time. The similar variation patterns in glycerol conversions and acrolein selectivities as a function of TOS provide a solid evidence that the initial low acrolein selectivities are due to that the system is not in dynamic stability, instead of rapid coke formation as proposed by Dalil et al.²⁹ These results also infer that
2 wt% coke deposition on the 3% NbWO₃/ZrO₂-450 catalyst does not significantly vary the acid/base active sites and has negligible influence on the catalyst activity.

### 3.4 Catalytic active sites

Zirconia is considered to be one of the amphoteric oxides and contains both acidic and basic sites on its surface. Addition of WO₃ to zirconia was found to significantly decrease the amount of basic sites and slightly increase the acidic sites. When used as the catalysts in gas-phase dehydration of glycerol, ZrO₂ gave complicated products with acetol (also known as hydroxylacetone, HA) as the largest portion of products (25% selectivity), while WO₃/ZrO₂ gave acrolein of 70% selectivity as the main product. Kinage et al. studies Na-doped metal oxides as the catalysts for glycerol conversion and proposed that the basic sites were responsible for HA formation. Chai et al. suggested that the strong acidic sites of Hammett constant in -8.2 to -3.0 were more efficient than those of medium to weak acid sites in acrolein formation. Besides, Lewis acids such as Al₂O₃ and Nb₂O₅ showed lower acrolein selectivities (ca. 40 mol%) than the materials containing Brønsted acids, such as supported phosphoric acid and heteropoly acid (60–70 mol%). On the other hand, the polyglycerols or acetalization products of glycerol were considered to form and be adsorbed on basic sites.

In our case, the glycerol consumption rate increases almost linearly with both amounts of acid and base sites, based on the Table 4 Product distributions in glycerol dehydration over WO₃/ZrO₂-450 with and without Nb₂O₅ doping.

| Catalysts            | Conversion (%) | Acrolein | AD  | AA  | HA  | Unknowns |
|----------------------|---------------|----------|-----|-----|-----|----------|
| WO₃/ZrO₂-450        | 99 (28)       | 68 (70)  | 6 (6)| 1 (3)| 9 (15)| 16 (6)   |
| 1% NbWO₃/ZrO₂-450   | 99 (77)       | 69 (70)  | 8 (5)| 2 (2)| 11 (14)| 10 (9)   |
| 3% NbWO₃/ZrO₂-450   | 99 (81)       | 69 (72)  | 7 (5)| 1 (2)| 9 (15)| 14 (6)   |
| 5% NbWO₃/ZrO₂-450   | 99 (74)       | 71 (70)  | 8 (5)| 2 (3)| 11 (17)| 8 (5)    |

*Reaction conditions: 290 °C, 0.3 g catalyst, GHSV = 1117 h⁻¹, 60 mL min⁻¹ N₂ flow rate. AD = acetaldehyde; AA = allyl alcohol; HA = 1-hydroxylacetone; selectivity for unknowns = (100 - known products)%. The selectivity data were data obtained at TOS = 3–4 h, and those in parenthesis obtained at TOS = 23–24 h of reaction.

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**Fig. 6** Correlations of (A) specific glycerol consumption rates, (B) acrolein yields, and (C) decay rates (average in 3–12 h TOS) with total acidic/basic sites on WO₃/ZrO₂ calcined at 400 to 700 °C (acid ■; base □), or NbWO₃/ZrO₂ catalysts (acid ★; base ★).
catalytic results of WO₃/ZrO₂ calcined at different temperatures (Fig. 6A). Nevertheless, there are optimal amounts of acid and base sites to obtain the maximum acrolein yield (Fig. 6B), which are 31–33 × 10¹⁸ sites per g catal for acidic sites and 7–12 × 10¹⁸ sites per g catal for basic sites. This is in consistence with the observation by Stošić et al.³⁰ that the selectivity of acrolein is largely governed by the balance between acidic and basic active sites. Fig. 6 also shows that when 1–5% Nb₂O₅ is doped in WO₃/ZrO₂-450, the acid amounts retain at relatively high values of 30–35 × 10¹⁸ sites per g catal, while the base amounts are shrunken in a narrower range of 7.5–8 × 10¹⁸ sites per g catal. Both are still in the range of the optimal amounts of acid and base sites to obtain the optimal acrolein yield.

In our case, most of the acidic sites on WO₃/ZrO₂-450 with and without doping Nb₂O₅ determined by pyridine adsorption are Lewis acid sites and the Brønsted acid sites are few and relatively weak. Therefore, Lewis acid sites seem to be the active sites for glycerol dehydration, and around 70% selectivities of acrolein are obtained. This finding is different from the literature reports that Lewis acids showed lower selectivities in the acrolein production than the materials containing Brønsted acids.³³ However, under the reaction condition where a large amount of water is present, it cannot be excluded that some Brønsted acidity may be generated through coordinative interaction of water molecules with Lewis acid sites on the catalysts. On the other hand, Kinage et al.³² proposed that the basic sites were responsible for hydroxylacetone (HA) formation. Indeed, higher HA selectivities are obtained on the catalysts containing larger amounts of basic sites, such as WO₃/ZrO₂-400 and WO₃/ZrO₂-450 (Table 3).

As the decay rate is concerned, Fig. 6C shows that it decreases almost linearly with both amounts of acid and base sites, and those trends are in reverse to those of glycerol consumption rate. WO₃/ZrO₂-400 is the most stable catalyst among WO₃/ZrO₂ calcined at different temperatures (Fig. 3 and Table 3), while WO₃/ZrO₂-800 which contains lowest amounts of acid sites and almost no basic sites gives the lowest glycerol conversion, acrolein selectivity and faster decay rate. Since the acid sites, which are active for glycerol dehydration, are also active for coke formation, the fast decay rate observed over WO₃/ZrO₂-800 should be due to coking on the active sites. With the increasing amount of basic sites on WO₃/ZrO₂ catalysts, the decay rate slows down. Therefore, basic sites should contribute the suppression of coke formation.

For Nb-doped WO₃/ZrO₂-450, the product selectivities in 3–4 h TOS are almost unaffected upon Nb-doping, while the Unknowns selectivities decrease with decreasing the amount of basic sites. It has been proposed that too many basic sites would lead to formation of macromolecules, such as polyglycerols or acetalization products of glycerol.³³,³⁴ Therefore, fine tuning the amount of basic sites is important. This conclusion is demonstrated in Fig. 6, in which the glycerol consumption rate, acrolein selectivity and catalyst decay rate all vary more drastically with the base amount than acid amount, and the optimal acrolein selectivity is obtained in a narrower range of base amount than that of acid amount.

Fig. 6E (ESI†) intends to correlate glycerol consumption rate, acrolein yield, and catalyst decay rate as a function of acid and base densities on the surface in the unit of sites per nm². No good correlation can be drawn, implying that the catalytic performance is less affected by the acid and base densities on the surface.

Fig. 7 correlates the catalytic performances with the ratio of acid/base sites. It shows the best performances are over Nb-doped WO₃/ZrO₂-450 catalysts which have acid/base ratios of 4.0–5.4. It is also noticed that there appears a narrow range of acid/base ratios of 3.25–3.5 giving lowest glycerol consumption rate, low acrolein yield, and fast catalyst decay rate. These results demonstrate again that fine tuning the ratio of acid/base sites is important in achieving good catalytic performance in gas-phase dehydration of glycerol to generate acrolein.

![Fig. 7](image-url) Correlations of (A) specific glycerol consumption rates, (B) acrolein yields, and (C) decay rates (average in 3–12 h TOS) with acidic/basic ratios on WO₃/ZrO₂ calcined at 400 to 700 °C (■) or NbWO₃/ZrO₂ catalysts (○).
4. Conclusions

Total amounts of acid and base sites of WO₃/ZrO₂ catalysts prepared by impregnation method decreased with the increase of calcination temperature. In gas-phase dehydration of glycerol, the glycerol consumption rate increased almost linearly with both amounts of acid and base sites. Nevertheless, the decay rate of the catalysts slowed down with the increase of total amounts of acid and base sites. The most suitable calcination temperature for WO₃/ZrO₂ catalyst was 450 °C in consideration of high acrolein yield and long lifetime of the catalyst. Furthermore, the deactivation of the catalyst could be greatly improved by doping small amount of niobium. Most of the acidic sites on WO₃/ZrO₂-450 with and without doping Nb₂O₅ are Lewis acid sites and the Brønsted acid sites are few and relatively weak. The optimal catalytic performance was kept at 82% acrolein yield which have acid/base ratios of 4.0–4.5. A spent catalyst could be easily regenerated by calcination at 450 °C for 3 h, and the catalytic activities were well retained.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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