Ruthenium catalysts supported on high-surface-area zirconia for the catalytic wet oxidation of *N,N*-dimethyl formamide

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Abstract

Three weight percent ruthenium catalysts were prepared by incipient-wet impregnation of two different zirconium oxides, and characterized by BET, XRD and TPR. Their activity was evaluated in the catalytic wet oxidation (CWO) of *N,N*-dimethyl formamide (DMF) in an autoclave reactor. Due to a better dispersion, Ru catalyst supported on a high-surface-area zirconia (Ru/ZrO$_2$-A) possessed higher catalytic properties. Due to over-oxidation of Ru particles, the catalytic activity of the both catalysts decreased during successive tests. The effect of oxygen partial pressure and reaction temperature on the DMF reactivity in the CWO on Ru/ZrO$_2$-A was also investigated. 98.6% of DMF conversion was obtained through hydrothermal decomposition within 300 min at conditions of 200 °C and 2.0 MPa of nitrogen pressure. At 240 °C and 2.0 MPa of oxygen pressure 98.3% of DMF conversion was obtained within 150 min.
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1. Introduction

Industry creates large annual amounts of wastewater containing products hazardous to the environment, and thus development of efficient technologies is needed. Considerable research efforts are being devoted into this field. Over the last years, wet air oxidation (CWAO) has emerged as a well-established proven technology for the treatment of streams with organic loads of 10–100 g l^{-1}, which are too toxic for biodegradation or too diluted for incineration [1]. In spite of the operating costs (high temperature and pressure), the catalytic wet air oxidation (CWAO) in the presence of a catalyst (oxides, noble metals, etc.) appears as one of the more promising wastewater treatment technology [2], which not only makes it possible to reduce the reaction temperature and pressure, but also avoids the formation of harmful products by complete oxidation of organic contaminants to harmless carbon dioxide, water and nitrogen [3].

N,N-Dimethyl formamide (DMF) is polar solvent widely used in chemical laboratories and in industrial manufactures of synthetic fibers, leathers and films [4,5]. The biological studies have shown that inhalation or dermal absorption of DMF in humans causes gastric irritation, pancreatic disorder and hepatotoxicity [6]. In 1989, DMF was classified in group 2B (possibly carcinogenic to humans) by International Agency for Research on Cancer (IARC) of the World Health Organization [7]. However, there is not so much attention paid to remove the toxicant by CWAO. Only Dobrynkin et al. [8] and Batygina et al. [3] investigated the activities of supported Ru catalysts in the CWAO of DMF; and Ru active carbon γ-Al$_2$O$_3$ was found to be very effective with 100% conversion and 100% selective to N$_2$ at 493 K [3].

Some studies have also shown that supported ruthenium catalysts were active and resistant to leaching for the wet air oxidation of many compounds such as acetic acid [9,10], ammonia [11,12] and chlorophenol [13]. The readily available stable materials for supporting ruthenium are usually TiO$_2$ [1,9,11,14], ZrO$_2$ [1,9,13] and CeO$_2$ [9,10]. Among the desired properties of a support, high-surface area and thermal stability rank very high. But the commercially available zirconium has typically less than 100 m^2 g^{-1} [9,15]. It has been shown that digestion

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of hydrous zirconia, which is the initial product from precipitation of zirconia salts, improved several properties of the calcined product zirconia, such as increased surface area, improved thermal stability, etc. [15,16]. The present work is related to CWAO of DMF over Ru catalysts supported on high-surface-area zirconia that were prepared by digestion of hydrous zirconia in the mother liquor. The effect of the oxygen pressure and reaction temperature was also investigated.

2. Experimental

2.1. Catalysts preparation

Zirconium oxides were prepared following a similar procedure described in reference [15]. A 5 wt.% aqueous solution of zirconium chloride was first prepared, and then 25% aqueous ammonia was added dropwise to this solution under stirring at room temperature until the resulting solution pH leveled off at 10. The formed hydrous zirconia was divided into two portions; one was subjected to digestion at 90 °C for 60 h while the other was left to age at room temperature for 60 h. After that the solids were recovered and washed free of chloride, followed by drying at 90 °C for 8 h and calcination at 450 °C for 2 h. The obtained ZrO_2 were then grinded to powder. The zirconium oxides from digestion and aging were referred to as ZrO_2-A and ZrO_2-B, respectively.

Three weight percent Ru/ZrO_2 catalysts were prepared by incipient-wet impregnation using aqueous solution of $RuCl_3$. The preparations were then dried at 120 °C in air for 12 h, introduced in a quartz tube reactor and reduced in flowing hydrogen at 350 °C for 3 h. The Ru/ZrO_2 catalysts using the supports ZrO_2-A and ZrO_2-B were referred to as Ru/ZrO_2-A and Ru/ZrO_2-B, respectively.

2.2. Catalyst characterization

BET surface areas were assessed by N_2 adsorption isotherms at 77 K using a ChemBET-3000 instrument. The catalyst samples prior to the adsorption measurement were degassed at 300 °C for 6 h under vacuum.

X-ray diffraction (XRD) patterns of the catalysts were analyzed with a Rigaku D/max RA diffractometer using Cu radiation at 50 kV and 100 mA.

Temperature programmed reduction (TPR) were carried out using 5% H_2/Ar gas mixture on a Micromeritics TPD/TPR 2900 instrument. The samples were pretreated with Ar at 350 °C for 30 min. The reactor was heated from room temperature to 800 °C at a heating rate of 5 °C min^{-1}.

2.3. Oxidation procedure

Catalyst testing was carried out in a 250 ml autoclave reactor made of titanium alloy at constant temperature and oxygen pressure as described in [17,18]. The reactor was loaded with 150 ml of 2.61 g l^{-1} DMF solution and a given mass of catalyst. When the set temperature was attained, the stirrer was started at a speed of 800 rpm. This time was taken as the zero time

of reaction. Liquid samples were periodically withdrawn from the reactor, filtered to remove any catalyst particle, and finally analyzed.

The substrates and the reaction intermediates in liquid phase were analyzed by a high performance liquid chromatography (HPLC) equipped with a Hypersil ODS2 column (4.6 mm × 250 mm) and an UV detector at 219 nm. A mixture of methanol (35%), deionized water (65%) and sulphuric acid (0.5%) was used as mobile phase at a flow rate of 1 ml min^{-1}. The total organic carbon (TOC) value was determined with a Shimadu TOC-V$_{CPH}$ analyzer. The ammonia-nitrogen was measured by Napierian reagent colorimetric method (GBZ50005-87). The total nitrogen was measured by alkaline potassium persulfate digestion-UV spectrophotometric method (GB 11894-89). Dimethyl amine (DMA) and the products such as CO and CO_2 in gas phase were analyzed by GC. The metal concentration in the final solution was analyzed by ICP-AES spectrometer, and no metal could be detected.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the bare ZrO_2 and the supported Ru catalysts. All the materials consist of a mixture of two phases: monoclinic ($2\theta = 28.5°$ and $31.6°$) and tetragonal ($2\theta = 30.4°$). No diffraction peak of the ruthenium phase could be observed indicating that Ru particles are probably well dispersed on the zirconia supports. The presence of amorphous RuO_2 species could cause the absence of Ru peaks. The zirconia from the digested precursor is predominantly tetragonal, but aging at room temperature results that zirconia crystallizes preferentially in the monoclinic phase. The results demonstrate that the crystal structure formed after precipitation can be altered by digestion [16].

The specific surface areas of the as-prepared solids are listed in Table 1. It can be seen that the surface area of ZrO_2-A is much larger than that of ZrO_2-B, as it has been proved that the zirconia formed from the digested hydrous oxides were better stabilized
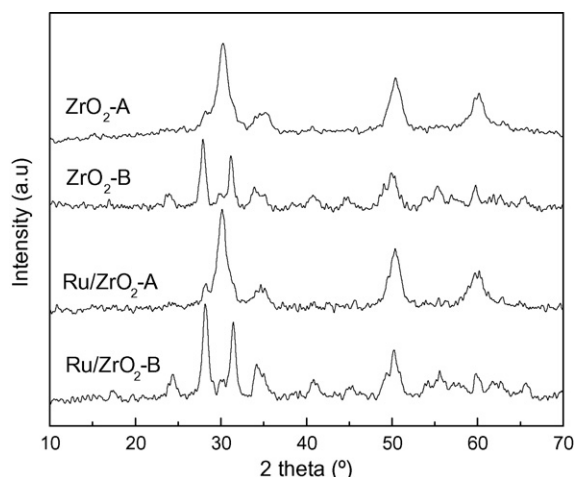

Fig. 1. XRD patterns of Ru/ZrO_2-A and Ru/ZrO_2-B.

Table 1
Activity of the Ru supported catalysts for DMF oxidation

Catalysts	Specific area ($m^2 g^{-1}$)	DMF conversion (%)	TOC removal (%)	TN removal (%)	pH
ZrO_2-A	191.4	30.2	9.70	19.6	9.63
ZrO_2-B	57.4	23.8	9.80	13.7	9.46
Ru/ZrO_2-A	123.6	55.0	18.0	28.9	9.41
Ru/ZrO_2-B	57.9	45.1	10.0	27.4	9.65
Blank	–	14.4	0	2.21	9.16

Reaction conditions: $T = 200\,°C$, $C_{DMF} = 2.61\,g\,l^{-1}$, pH 7.45, $C_{Cat} = 3.33\,g\,l^{-1}$, $P_{O_2} = 2.0\,MPa$ and time = 150 min.

against loss of surface area during calcination than that from undigested [16]. After impregnation with 3 wt.% Ru, a decrease in the specific area on the ZrO_2-A was observed, but was not on the ZrO_2-B.

Fig. 2 shows the hydrogen consumption by Ru solids as a function of temperature during the TPR experiments. For the Ru/ZrO_2-A catalyst, three peaks are observed: a wide reduction peak at 336.9 °C, a second one at 164.8 °C, and a third one at 123.7 °C. The Ru/ZrO_2-B profile is clearly different. A high intensity peak appears at 155.8 °C with a slight shoulder at 128.8 °C while a wide peak appears at 308.5 °C. According to some Refs. [19,20], the low-temperature peak (less than 140 °C) has been assigned to the reduction of well-dispersed RuOx species and the peak at about 160 °C has been attributed to RuO$_x$ particles. The high temperature peak at above 300 °C suggests the presence of a strong metal–support interaction. As the Ru/ZrO_2-B catalyst shows smaller area for the well-dispersed RuOx species reduction and larger area for the RuO$_x$ particles than the Ru/ZrO_2-A, it can be concluded that Ru catalyst supported on ZrO_2-A are more highly dispersed. That the high temperature peak for ZrO_2-B becoming smaller comparing with the peak at 336.9 °C for ZrO_2-A can be also observed. A likely explanation is that the Ru particles keep a closer contact with ZrO_2-A when the support has a high-surface area.

3.2. Activity of the ruthenium supported catalysts

The catalytic activity of the bare ZrO_2 and the supported Ru catalysts on CWAO of DMF was first studied at 200 °C under 2.0 MPa oxygen pressure. The evolution of the DMF conversion, the TOC removal, the total nitrogen removal and the pH of solution after 150 min of reaction was summarized in Table 1. As it is well known that DMF is little convertible in water solutions and its hydrolysis is fairly slow in absence of special conditions (catalyst, high temperature, etc.) [3], in blank experiment the DMF conversion is very low and no TOC removal was detected. The bare ZrO_2 possess catalytic activity comparing with the blank experiment, and ZrO_2-A has higher activity owing to its high-surface area. Supported Ru catalysts are more active than the bare ZrO_2 as usually observed; and due to a better dispersion Ru/ZrO_2-A shows the highest catalytic properties. However, the yield of CO_2 over this catalyst is still very low.

Selectivity towards N_2 is a key factor characterizing catalyst work on CWAO of nitrogen-containing wastes. Some literatures reported that supported Ru catalysts were highly selective for catalytic oxidation of DMF [3] and NH_3 [11,12] to N_2 even at low temperatures. However, in our experiment at these conditions the selective formation of N_2 is very low, as the highest total nitrogen conversion in liquid phase after reaction is only 28.9% for Ru/ZrO_2-A catalyst. The initial pH of the DMF solution is around 7.45. After reaction the pH of the solution increases remarkably. The increase of the basicity is directly connected with the degradation of the formation of some basic reaction intermediates such as $HN(CH_3)_2$ and NH_3. Generally, the higher the DMF conversion, the higher the solution pH. But this is not true for Ru/ZrO_2-A as the catalyst shows faster degradation rate of the basic intermediates as discussed latter.
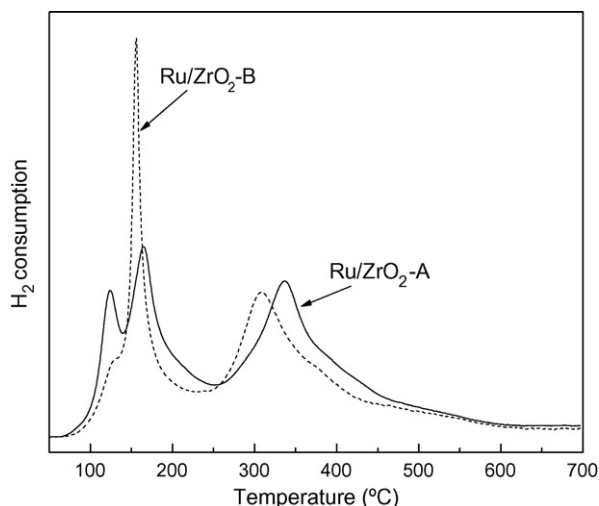

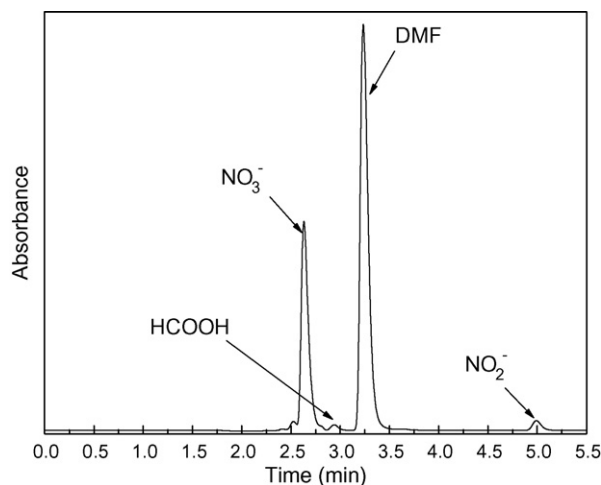Fig. 2. H_2-TPR profiles of Ru/ZrO_2-A and Ru/ZrO_2-B.

Fig. 3. Typical products detected by HPLC from Ru/ZrO_2-A at conditions of 200 °C and 2.0 MPa oxygen pressure with 150 min.

According to the scheme of DMF oxidation proposed by Batygina et al. [3], the first reaction step is hydrothermal decomposition of DMF to $HN(CH_3)_2$ and $HCOOH$. $HN(CH_3)_2$ can be then converted to CO_2 and NH_3 or other nitrogen compounds, depending on the catalyst and reaction conditions; and $HCOOH$ to CO_2. In this paper the intermediates detected by HPLC in the liquid phase include $HCOOH$, NO_3^-, and NO_2^- (shown in Fig. 3). NH_3 was detected by napierian reagent colorimetric method. Among the five reactions, a more noticeable difference was observed in the presence of Ru/ZrO_2-A catalyst, for it shows the lowest amount of $HCOOH$ and the highest of NO_3^-. This means that $HCOOH$ and NH_3 can be easier oxidized on this catalyst.

Three recycling operations were also carried out to examine the stability of Ru/ZrO_2-A and Ru/ZrO_2-B catalysts. Starting from the fresh catalyst, four experiments of DMF oxidation were conducted with the same catalyst recycled after separation. The recovered catalyst was reused as such for the oxidation of fresh solution. The DMF conversion after 150 min is given in Fig. 4. During the four experiments the activity of Ru/ZrO_2-A is higher than that of Ru/ZrO_2-B throughout. But for the both catalysts their activity slightly decreased after the second catalyst recycle, then was stable after the third recycle. But during the successive tests later on their activity decreased again. The deactivation can be attributed to the over-oxidation of small Ru particles
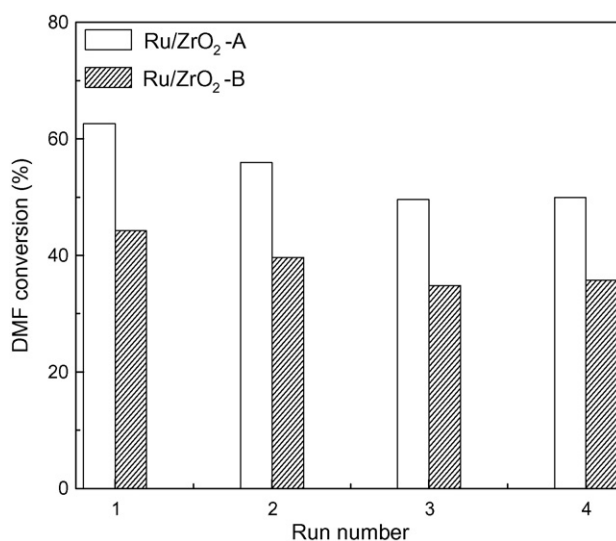

Fig. 4. DMF conversion with Ru/ZrO_2-A and Ru/ZrO_2-B catalysts after three recycling operations ($T = 200\,°C$, $C_{Cat} = 6.67\,g\,l^{-1}$, $P_{O_2} = 2.0\,MPa$ and time = 150 min).

on catalyst surface [21,22], as the loss of activity was completely reversible upon catalyst reduction in hydrogen (shown in Table 2). The supported Ru catalysts are stable against fouling, sintering and leaching [21].
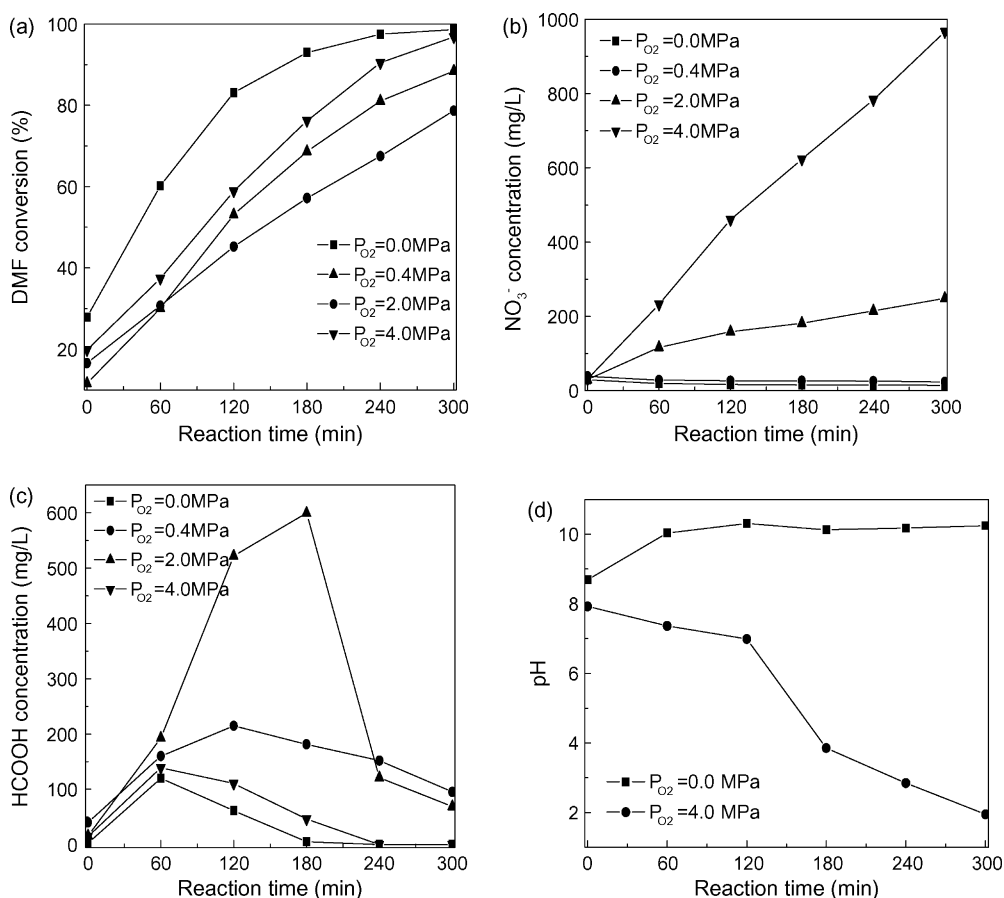

Fig. 5. CWAO of DMF over Ru/ZrO_2-A at different oxygen pressures: (a) DMF conversion; (b) NO_3^- concentration; (c) $HCOOH$ concentration; (d) solution pH. ($T = 200\,°C$ and $C_{Cat} = 3.33\,g\,l^{-1}$).

Table 2
DMF conversion during successive tests in CWAO over Ru/ZrO$_2$-A catalyst

Run time	DMF conversion (%)
5	48.5
6	46.2
7	43.8
8[a]	43.2
9[b]	60.6

[a] The catalyst was treated by N$_2$H$_4$ solution at 100 °C.
[b] The catalyst was treated by H$_2$ at 350 °C.

3.3. Effect of oxygen pressure on catalytic behavior of Ru/ZrO$_2$-A for DMF oxidation

Owing to the good performance of supported Ru catalyst on the high-surface-area zirconia in DMF oxidation, it was decided to investigate further the catalytic behavior under a group of designed operation conditions, including oxygen pressure and temperature. The DMF conversion, the amount of NO$_3^-$ and HCOOH, and the solution pH were shown to assess the reaction results.

The effect of oxygen partial pressure in the range of 0–4.0 MPa was firstly examined, as shown in Fig. 5(a)–(d). Contrary to the normal impact of oxygen partial pressure on the mineralization of many organic pollutants upon CWAO [13,14,23,24], in Fig. 5(a) it was observed that below 4.0 MPa DMF conversion increases with decreasing oxygen pressure. This effect is tentatively correlated to the high catalytic hydrolytic rate of DMF at low oxygen pressures. Generally, the hydrolytic products of DMF are HCOOH and HN(CH$_3$)$_2$. When the reaction was carried out under nitrogen ($P_{O2} = 0$ MPa), large amount of HN(CH$_3$)$_2$ and NH$_3$ was detected as prediction; but the detected HCOOH was very low (shown in Fig. 5(c)). Therefore, in this case it can assume that the hydrolysis reaction was promoted by Ru/ZrO$_2$-A catalyst through decomposing HCOOH into some products such as CO and/or CO$_2$ [25]; and the presence of CO confirmed our assumption.

At high oxygen partial pressure (ca. $P_{O2} = 4.0$ MPa), the hydrolytic products can be further oxidized by Ru/ZrO$_2$-A into CO$_2$ and NO$_3^-$, as shown in Fig. 5(b) and (c), leading to the right shift of the hydrolysis balance. In Fig. 5(b), the concentration of NO$_3^-$ increases with increasing oxygen pressure; and in Fig. 5(c), below 4.0 MPa the HCOOH concentration also increases with increasing oxygen pressure. The detected small concentration of HCOOH at 4.0 MPa of oxygen pressure was caused by the fast oxidation of this product into CO$_2$ in this condition.

The solution pH profiles shown in Fig. 5(d) give another evidence of the above explanation. Under nitrogen atmosphere the solution pH is at above 10, indicating the great produce of HN(CH$_3$)$_2$ and NH$_3$; but at 4.0 MPa of oxygen atmosphere the solution pH decreases from 7.93 to 1.95 with increasing reaction
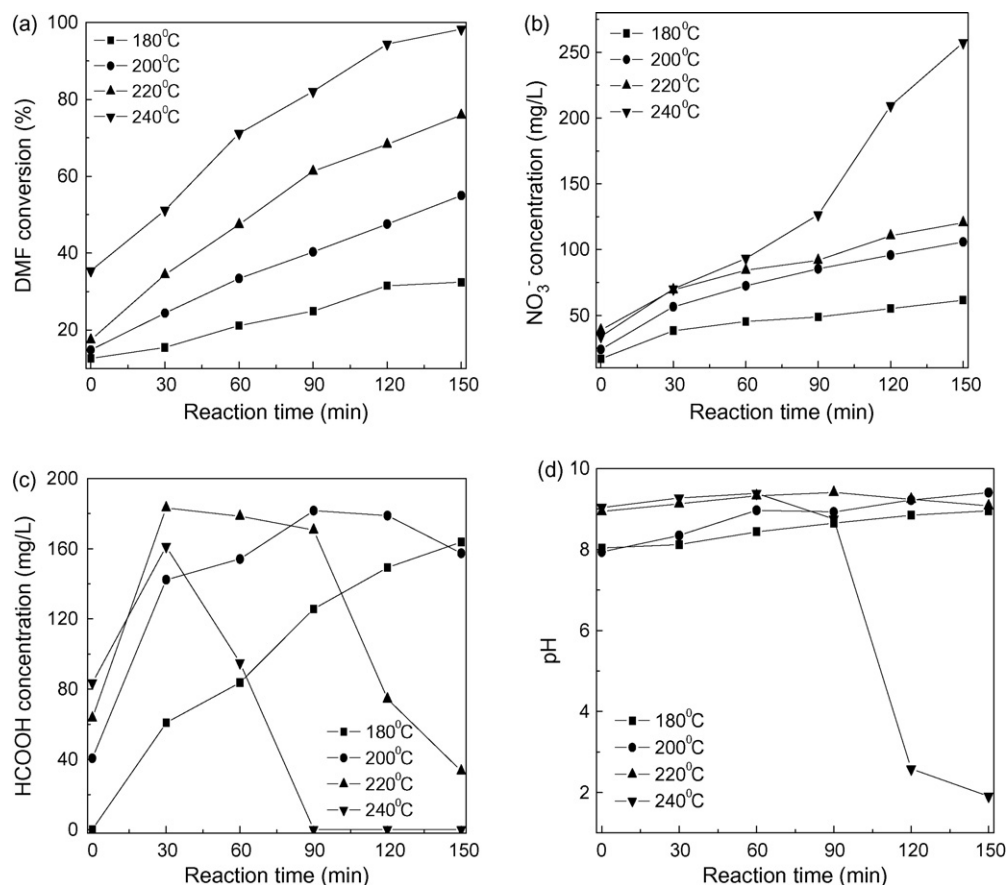

Fig. 6. CWAO of DMF over Ru/ZrO2-A at different reaction temperatures: (a) DMF conversion; (b) NO$_3^-$ concentration; (c) HCOOH concentration; (d) solution pH ($C_{Cat} = 3.33$ g l^{-1} and $P_{O_2} = 2.0$ MPa).

time, indicating that $HN(CH_3)_2$ and NH_3 were further oxidized to HNO_3.

3.4. Effect of reaction temperature on catalytic behavior of Ru/ZrO₂-A for DMF oxidation

As discussed in Table 1, the conversion of DMF and the selective formation of N_2 are very low for Ru/ZrO₂-A catalyst at 200 °C. In this section some experiments were carried out under higher reaction temperatures in order to determine the optimum reaction conditions of the complete transformation and mineralization of DMF to harmless products. Fig. 6(a) shows the effect of reaction temperature on DMF conversion. It can be seen the rate of disappearance of DMF increases at increasing temperature. At 240 °C, a 98% DMF conversion was reached after 150 min. At zero time the observed DMF conversion is high, but it cannot be concluded immediately that DMF is mainly adsorbed on the catalyst, as the amount of products at this time is also high (shown in Fig. 6(b) and (c)).

Fig. 6(b) shows the results of detected nitrate concentration. It appears that the nitrate concentration increases when increasing the reaction temperature; but the increased value is not too large. The highest concentration is 257 mg/l obtained at 240 °C after 150 min, only occupying 11.8% in total conversed nitrogen. This means that a high selective formation of N_2 (about 88%) is obtained in this case, as the other forms of conversed nitrogen such as $HN(CH_3)_2$, NH_3 and NO_2^- were not detected. Fig. 6(c) shows the results of detected HCOOH concentration. It can be seen that at low reaction temperature (ca. 180 °C), the amount of HCOOH increases with reaction time, indicating the product is resistant to oxidation at this temperature. At higher temperatures, its amount first increases and then decreases. The higher the temperature, the faster it disappeared. Fig. 6(d) compares the solution pH detected under different reaction temperatures. As can be observed the solution pH profiles show similar trends with that of HCOOH concentration in Fig. 6(c). The most noticeable observation is that at 240 °C the solution pH rapidly decreases to 1.91 after 150 min, implying that the basic reaction intermediates has completely disappeared.

4. Conclusions

The ZrO₂-A prepared by digestion of hydrous zirconia in the mother liquor has a high-surface area of $191.4 \, m^2 \, g^{-1}$, which is larger than the ZrO₂-B prepared from aging. Ru catalyst supported on the high-surface-area zirconia (Ru/ZrO₂-A) with a better dispersion was confirmed by TPR. Among all the as-prepared solids Ru/ZrO₂-A possesses the highest catalytic activity in CWAO of DMF. The intermediates detected by HPLC in the liquid phase include HCOOH, $HN(CH_3)_2$, NH_3, NO_3^- and NO_2^-. The strong influence of the oxygen pressure and reaction temperature on DMF oxidation is clearly demonstrated. At low oxygen pressure Ru/ZrO₂-A catalyst promotes DMF hydrolysis rate through decomposing HCOOH into some products. At 240 °C and 2.0 MPa of oxygen pressure 98.3% of DMF conversion is obtained within 150 min; and a high

selective formation of N_2 (about 88%) is also obtained in this case.

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