

# Surface properties and CO adsorption on zirconia polymorphs

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## Abstract

FT-IR spectroscopy and TPD profiles were performed to determine and compare the surface properties of amorphous, monoclinic and tetragonal zirconia polymorphs. It was found that zirconia polymorphs exhibited different surface hydroxyl and acid–base properties. These differences had great influence on the behavior of CO adsorption and reaction. Formate species could be formed at higher temperature via CO reaction with hydroxyl groups on the surface of amorphous and monoclinic zirconia, while bicarbonate and carbonate species were detected on tetragonal zirconia, whether hydrogen introduced or not.

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*Keywords:* Zirconia; Surface hydroxyl; Acidity and basicity; CO adsorption

## 1. Introduction

During the last two decades, zirconia has attracted much attention due to its special surface chemical properties, i.e. both redox and acid–base properties [1]. As a result, zirconia acted not only as the supports but also an active component in most reactions [2–4]. For instance, Cu/ZrO<sub>2</sub> catalyst showed high catalytic performance for alcohol synthesis from CO<sub>2</sub>/CO hydrogenation [2], in which zirconia showed splendid synergetic effect with Cu. Bianchi et al. [3] reported that there existed the overflow of absorbed hydrogen and carbon monoxide in the interface of zirconia and copper. Fisher and Bell [4] proposed that methanol synthesis mainly performed on zirconia support by studying the surface intermediate species from CO/H<sub>2</sub> reaction on Cu/Zr/SiO<sub>2</sub>. Meanwhile, zirconia polymorphs had a great influence on catalytic performance for many reactions, which might be contributed to the different surface properties of various zirconia polymorphs [5,6].

Zirconia surface contained Brønsted acidic and basic hydroxyl groups and co-ordinatively unsaturated Lewis acid–base Zr<sup>4+</sup>–O<sup>2-</sup> pairs. These surface hydroxyl groups

were sensitive towards the surface structure, which were conveniently studied by infrared spectroscopy [7–11]. But there raised the arguments about the nature of hydroxyl which was caused by zirconia polymorphs. Yamaguchi et al. [11] considered that two types of hydroxyl existed on zirconia surface and the terminal hydroxyl was more active and liable than that of bridged one. However, Guglielminotti [12] argued that there was no apparent difference in reactivity for hydroxyl groups in the case of CO hydrogenation. Bachiller-Baeza et al. [13] found that another hydroxyl band located at about 3740 cm<sup>-1</sup>, which could be contributed to bi-bridged hydroxyl, only existed on tetragonal zirconia surface. Thus, the systematic research should be performed to determine and compare the surface hydroxyl on zirconia polymorphs at same treatment condition.

On the other hand, surface acid–base sites were associated with the CO and CO<sub>2</sub> adsorption and then played an important role in catalytic performance. These surface sites were produced during thermal dehydroxylation of metal oxides, depending on their co-ordination symmetry. Hence, the acid–base properties of zirconia have been studied by the adsorption of probe molecules such as CO, CO<sub>2</sub>, pyridine and NH<sub>3</sub> in the literatures [7,14–16]. Lewis acid sites were more abundant on monoclinic zirconia than on tetragonal zirconia, and the former brought about stronger surface adsorption sites

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concerning CO<sub>2</sub> adsorption than the latter [13]. Two distinct Lewis acid sites have been observed on the zirconia surface revealed by FT-IR of CO adsorption, which were assigned to two Zr<sup>4+</sup> cations, co-ordinatively unsaturated, exposed either at different crystallographic or with different co-ordinative unsaturations [15]. While the weak acid sites of Zr<sup>3+</sup> was only detected on monoclinic zirconia by the vacuum thermal condensation of surface hydroxyls [16].

In view of the importance of the surface properties of zirconia, particularly in the field of CO hydrogenation, the adsorption of CO, CO<sub>2</sub>, pyridine and NH<sub>3</sub> over zirconia polymorphs was systematically carried out in the present work. The main goal was to detect the influence of zirconia polymorphs on the surface acid–base properties, and the relation between surface hydroxyl groups with acid–base sites. Also, we considered, whether the differences in surface properties had some contribution to CO adsorption and reaction in the presence or absence of hydrogen.

## 2. Experimental

### 2.1. Sample preparation

Amorphous zirconia (am-ZrO<sub>2</sub>) was prepared from a solution of oxychloride zirconium co-precipitation with ammonia. After aging in the mother liquid for 3 h, the gel was washed and filtered with distilled water until chloride test negative for AgNO<sub>3</sub>. Then the precipitate was dried at 393 K for 12 h and calcined at 623 K for 3 h. The precipitate prepared as above was aged in the mother liquid at 323 K for 5 days, and then filtered, dried and calcined at 823 K for 3 h, the sample was characterized by XRD to prove as monoclinic zirconia (m-ZrO<sub>2</sub>). The tetragonal zirconia (t-ZrO<sub>2</sub>) was prepared by co-precipitating a solution of oxychloride zirconium and sodium carbonate, followed similar filtering and drying to am-ZrO<sub>2</sub> and m-ZrO<sub>2</sub>, and then calcined at 823 K for 3 h. XRD patterns showed that am-ZrO<sub>2</sub> was only a broad peak at 30° while the diffraction peaks of monoclinic and tetragonal zirconia were predominant. The BET surface areas of am-ZrO<sub>2</sub>, m-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> determined by N<sub>2</sub> adsorption were 214.5, 41.46 and 26.91 m<sup>2</sup> g<sup>-1</sup>, respectively.

### 2.2. Characterization methods

NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD were carried out on a U-shape quartz reactor. 0.2 g sample was pre-treated in an Argon flow at 573 K for 4 h. After cooling to certain temperature, the sample was saturated with NH<sub>3</sub> (373 K) or CO<sub>2</sub> (RT), and then purged for 30 min to sweep the physical molecules. Hereafter, the sample was heated to 773 K in an Ar flow at rate of 10 K min<sup>-1</sup>. The desorbed NH<sub>3</sub> and CO<sub>2</sub> were monitored by a Balzers Omnistar 200 mass spectroscopy.

Pyridine adsorption (Py-FT-IR) was performed on the Nicolet Magna-II 550 FT-IR spectrometer equipped with TGS detector. About 15 mg sample was pressed to a Φ15 mm

self-supporting wafer and treated in a quartz cell with CaF<sub>2</sub> windows at 573 K and 10<sup>-3</sup> Pa for 2 h. A background spectrum was collected at room temperature before the pyridine was introduced. Then the sample was evaporated at 423 K for 30 min to remove physical pyridine, and another spectrum was collected at resolution of 4 cm<sup>-1</sup> and 64 times. The difference spectrum was obtained by subtraction with background spectrum.

CO and CO/H<sub>2</sub> diffuse reflectance FT-IR (DRIFT) were recorded using Nicolet Magna-II 550 FT-IR spectrometer equipped with Spectra-Tech Diffuse Reflectance Accessory and a high temperature in situ cell with ZnSe windows. A KBr beam splitter had been used with a TGS detector. One set of stainless steel lines was built and connected to the cell. This allowed in situ measurement for adsorption in a flow of gas. Powder sample was patched on the cell and then treated at 573 K in an Argon flow for 4 h. CO (99.999%) or CO/H<sub>2</sub> (1:2 molar ratio) was introduced at 623 K for 15 min. After system cooling down to room temperature, the spectrum was collected at resolution of 8 cm<sup>-1</sup> and 400 scans. Each spectrum was then referenced to a spectrum of the catalyst collected at the same temperature under Argon flow before adsorption, as appropriate.

## 3. Results and discussion

### 3.1. Surface properties

It was shown that on the surface of highly hydrated zirconia, co-ordinated molecular water was eliminated upon evacuation at 450 K and various types of surface hydroxyls remained up to 873 K [17]. Generally, three types of hydroxyl groups could be observed with bands at the region of 3770–3750 cm<sup>-1</sup>, 3750–3720 cm<sup>-1</sup> and 3660–3680 cm<sup>-1</sup> [6,11,18], which were ascribed to terminal, bi-bridged and tri-bridged hydroxyl groups, respectively. It was clearly indicated that there existed great difference in hydroxyl groups on the surface of zirconia polymorphs (see Fig. 1). Besides terminal and tri-bridged hydroxyls located at 3770 cm<sup>-1</sup> and

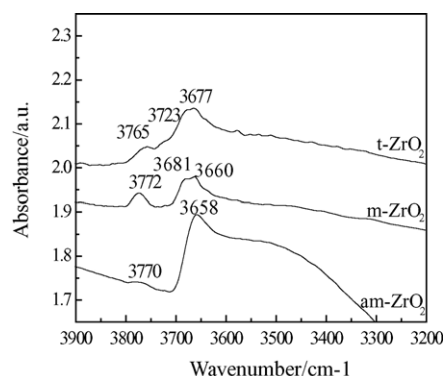


Fig. 1. Difference transmission infrared spectra of surface hydroxyls on three zirconia polymorphs vacuum activated at 573 K for 2 h.

3658  $\text{cm}^{-1}$ , respectively, a broad peak at 3500  $\text{cm}^{-1}$  was observed on the surface of am-ZrO<sub>2</sub>, which was attributed to the surface hydroxyl perturbed by hydrogen bond [19]. Three types of hydroxyl located at 3772, 3681 and 3660  $\text{cm}^{-1}$  existed on the surface of m-ZrO<sub>2</sub>, which could be ascribed to one type of terminal and two types of tri-bridge hydroxyls, respectively. The former tri-bridged hydroxyl might be located at crystallographic defective configurations and the latter belonged to the flat patches of low-index crystal planes [20]. While in the case of t-ZrO<sub>2</sub> terminal, bi-bridged and tri-bridged hydroxyls were detected at 3765, 3723 and 3677  $\text{cm}^{-1}$ . It was remarked that no bi-bridged hydroxyl was detected on monoclinic and amorphous zirconia polymorphs. Cerrato et al. [20] considered that, in the (1 1 1) crystal plane of monoclinic zirconia, the distance between *cus* O<sup>2-</sup> and *cus* Zr<sup>4+</sup> was only 0.2 nm and did not allowed the dissociation of a water molecule to form the terminal and bi-bridged hydroxyl groups. Therefore, the type of surface hydroxyl groups remaining upon evacuation depended strongly on the structural modification.

The identification of acid type could be achieved from FT-IR spectra after pyridine adsorption. Pyridinium ion (formed at Brønsted acid sites) displayed 1540  $\text{cm}^{-1}$  bands and coordinately bonded pyridine (formed at Lewis sites) gave 1445  $\text{cm}^{-1}$  bands [21]. Fig. 2 showed the difference FT-IR spectra of pyridine adsorption on three zirconia polymorphs after evacuation at 423 K. The bands located at 1445, 1580 and 1606  $\text{cm}^{-1}$ , corresponding to Lewis acid sites, were observed on three zirconia polymorphs, meanwhile, the band intensity decreased in the order of am-ZrO<sub>2</sub> > m-ZrO<sub>2</sub> > t-ZrO<sub>2</sub>. It was noted that there existed a weak band at 1537  $\text{cm}^{-1}$  only on m-ZrO<sub>2</sub>. These results reflected that Lewis acid sites presented on three zirconia polymorphs and the intensities were in the order of am-ZrO<sub>2</sub> > m-ZrO<sub>2</sub> > t-ZrO<sub>2</sub>, while Brønsted acid sites was only detected on the surface of m-ZrO<sub>2</sub>. Perhaps the Brønsted acid sites on the surface of am-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> were too weak to form pyridinium ion. Yubao Zhao et al. [14] also detected the weak Brønsted acid sites only on the surface of m-ZrO<sub>2</sub> using pyridine as probe, but Hertl [7] observed Brønsted acid sites on three zirconia polymorphs using NH<sub>3</sub> as probe molecule. In

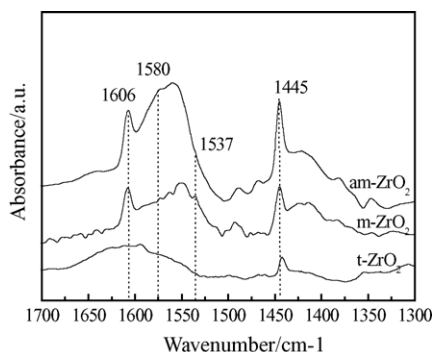


Fig. 2. Difference transmission infrared spectra of pyridine adsorbed on three zirconia polymorphs after evacuation at 423 K for 30 min.

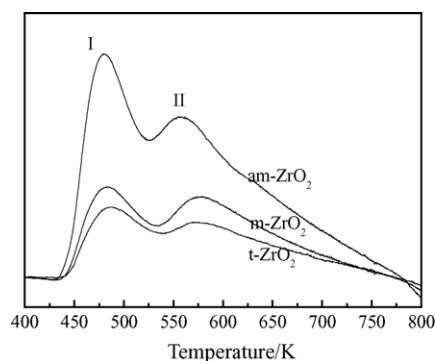


Fig. 3. NH<sub>3</sub>-TPD profiles of three zirconia polymorphs.

the hydroxyl region (Fig. 1), m-ZrO<sub>2</sub> showed strong terminal hydroxyl, which might be responsible for the strong Brønsted acid sites.

The acid sites distributions of three zirconia polymorphs were characterized by the NH<sub>3</sub>-TPD. Fig. 3 showed two NH<sub>3</sub> desorption peaks located at about 480 K and 570 K on three samples, corresponding to a weak acid sites I and a moderate acid sites II, respectively. For the acid sites I, the intensity was almost the same on three zirconia polymorphs, while the acid sites II on am-ZrO<sub>2</sub> was weaker than those on m-ZrO<sub>2</sub> and t-ZrO<sub>2</sub>. The amount of acid sites on am-ZrO<sub>2</sub> was higher than those on two others (see Table 1), and t-ZrO<sub>2</sub> had the smallest amount of acid sites, which was in line with the result of Py adsorption. Though the present value was about 1.55  $\text{nm}^{-2}$  NH<sub>3</sub> adsorbed on t-ZrO<sub>2</sub> and 1.88  $\text{nm}^{-2}$  NH<sub>3</sub> on m-ZrO<sub>2</sub>, the tendency that more acid sites existed on m-ZrO<sub>2</sub> was consistent with the literature [14].

Samples were further characterized by CO<sub>2</sub>-TPD to determine the base sites distribution (see Fig. 4). Two CO<sub>2</sub> desorp-

Table 1  
Acid sites density on three zirconia polymorphs<sup>a</sup>

Zirconia	Acidity sites I ( $\text{nm}^{-2}$ )	Acidity sites II ( $\text{nm}^{-2}$ )	Total acidity site ( $\text{nm}^{-2}$ )
am-ZrO <sub>2</sub>	1.09	2.80	2.89
m-ZrO <sub>2</sub>	1.07	0.81	1.88
t-ZrO <sub>2</sub>	0.81	0.74	1.55

<sup>a</sup> Calculated from NH<sub>3</sub> desorption.

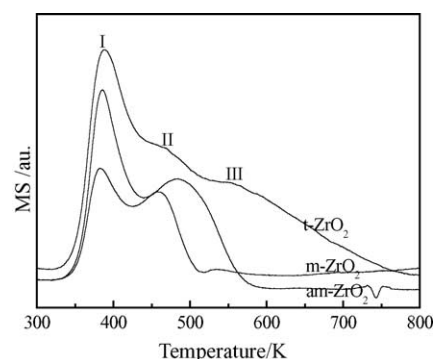


Fig. 4. CO<sub>2</sub>-TPD profiles of three zirconia polymorphs.

Table 2  
Base sites density on three zirconia polymorphs<sup>a</sup>

Zirconia	Basic sites I (nm <sup>-2</sup> )	Basic sites II (nm <sup>-2</sup> )	Basic sites III (nm <sup>-2</sup> )	Total basic sites (nm <sup>-2</sup> )
am-ZrO <sub>2</sub>	0.65	1.08	–	1.73
m-ZrO <sub>2</sub>	0.37	0.56	–	0.93
t-ZrO <sub>2</sub>	0.64	0.49	2.10	3.23

<sup>a</sup> Calculated from CO<sub>2</sub> desorption.

tion peaks located at low temperature and high temperature, corresponding to a weak base sites I and a moderate base sites II, were observed on am-ZrO<sub>2</sub> and m-ZrO<sub>2</sub>, respectively. But there existed another peak at higher temperature on t-ZrO<sub>2</sub> indicating a strong base sites III. For weak base sites I, the intensity was almost same for three zirconia polymorphs, but for the base sites II, the intensity decreased in the order of am-ZrO<sub>2</sub> > t-ZrO<sub>2</sub> > m-ZrO<sub>2</sub>. The total desorption CO<sub>2</sub> on t-ZrO<sub>2</sub> was almost 4 times higher than that on m-ZrO<sub>2</sub> (see Table 2). As a result, t-ZrO<sub>2</sub> showed much higher basicity than the two others.

### 3.2. CO adsorption

The DRIFT spectra of CO adsorbed onto three zirconia polymorphs were illustrated in Fig. 5. Two bands located at 2136 cm<sup>-1</sup> and 2197 cm<sup>-1</sup> were detected when CO adsorbed on am-ZrO<sub>2</sub> at 623 K (see Fig. 5B). The difference in wave number was as large as 60 cm<sup>-1</sup>, indicating that two sites had large difference in electronic intensity. Bolis et al. [15] considered that high ability of withdrawing electron of *cus* Zr<sup>4+</sup> resulted in CO band shifting to higher wave number. Thus, the band at 2197 cm<sup>-1</sup> could be ascribed to CO adsorption on *cus* Zr<sup>4+</sup>. On the other hand the band at 2136 cm<sup>-1</sup> could not be explained by the polarization of the carbon monoxide molecule in the electronic field of the surface. And the band might be attributed to CO interacting with surface hydroxyl groups via H-band [22], which was possibly evidenced by the hydroxyl disturbance location at 3500 cm<sup>-1</sup> (see Fig. 5A). When CO adsorbed on m-ZrO<sub>2</sub> at 623 K, only a band at 2109 cm<sup>-1</sup> could be observed (see Fig. 5B), probably due to CO adsorption on *cus* Zr<sup>3+</sup>, proved by Morterra et al. [16] using EPR spectroscopy. They also found other CO peaks located above 2160 cm<sup>-1</sup> on the surface of vacuum-activated m-ZrO<sub>2</sub>. But in the present work, there was no other band could be seen except the 2109 cm<sup>-1</sup> band. Vacuum thermal activity of metal oxides could cause gradual surface dehydration and, at higher temperatures, create surface co-ordinatively unsaturated *cus* Zr<sup>n+</sup> ions and co-ordinatively unsaturated anion–cation pairs. However, the sample was not undergone vacuum thermal treatment in the present work, which might result in the difference from the literature.

CO adsorption on t-ZrO<sub>2</sub> showed a weak band at 2183 cm<sup>-1</sup>, with a difference of 14 cm<sup>-1</sup> compared to CO band at 2197 cm<sup>-1</sup> on am-ZrO<sub>2</sub> (see Fig. 5B). Bolis [15] considered that two families of acid sites (Zr<sup>4+</sup>) existed on zirconia surface, which exhibited different acidic strength and stability. The high energetic sites (CO band

at 2197 cm<sup>-1</sup>) were contributed to low regular and less probable configurations, which could be exposed on rougher (high index) planes. The low energetic sites (CO band at 2180 cm<sup>-1</sup>) were ascribable to the flat face (low index).

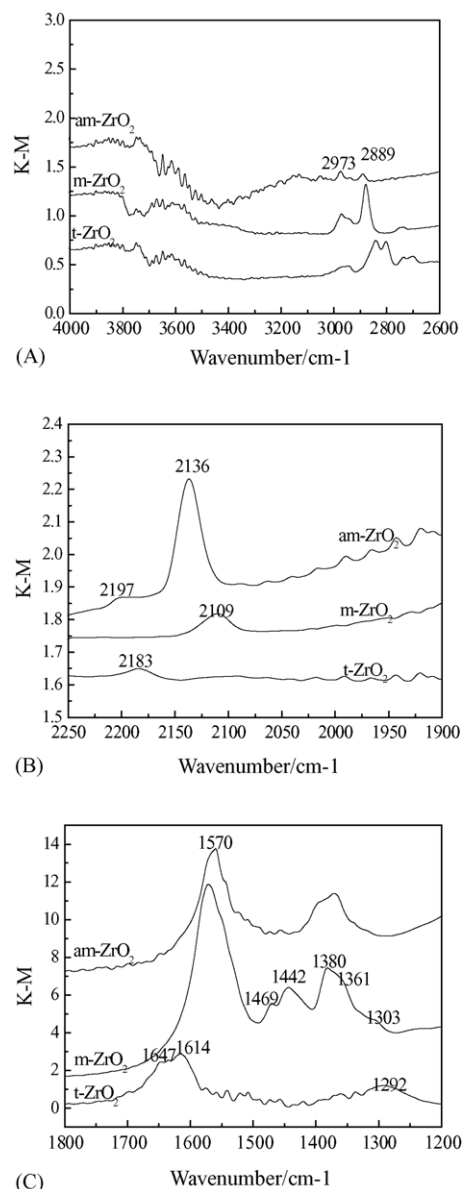


Fig. 5. Difference DRIFT spectra of CO adsorbed on three zirconia polymorphs. Section A: hydroxyl and  $\nu$ C–H region (4000–2600 cm<sup>-1</sup>); section B:  $\nu$ CO region (2250–1900 cm<sup>-1</sup>); section C: surface intermediates region (1800–1200 cm<sup>-1</sup>).

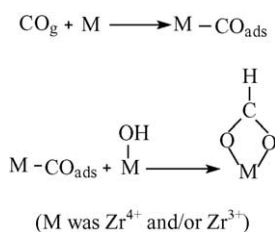
Thus, the acid sites on t-ZrO<sub>2</sub> were less energetic than that on am-ZrO<sub>2</sub>, then leading to lower wave number. And the low index sites possessed weak capacity of adsorption CO, which could be proved by the intensity of CO band at 2183 cm<sup>-1</sup> compared to the band at 2197 cm<sup>-1</sup>. On the other hand, the intensity of CO band decreased in the order of am-ZrO<sub>2</sub> > m-ZrO<sub>2</sub> > t-ZrO<sub>2</sub>, which was in accordance with the intensity of surface Lewis sites determined by Py adsorption.

Intermediate species were observed in the region of 1800–1200 cm<sup>-1</sup> when CO adsorbed on zirconia polymorphs (see Fig. 5C). As CO adsorbed on am-ZrO<sub>2</sub> at 623 K, the formate species was well identified by the bands located at 1570 (ν<sub>as</sub>OCO), 1380 (δCH) and 1361 cm<sup>-1</sup> (ν<sub>s</sub>OCO), the difference of 200 cm<sup>-1</sup> between the symmetric (1361 cm<sup>-1</sup>) and anti-symmetric (1570 cm<sup>-1</sup>) stretching mode of OCO tended to show that the formate was rather bidentate than monodentate. In the case of m-ZrO<sub>2</sub>, the infrared spectra were relatively complicated compared to am-ZrO<sub>2</sub>. Besides the formate bands located at 1570, 1380 and 1361 cm<sup>-1</sup>, the bands at 1469, 1303 cm<sup>-1</sup> and 1442 cm<sup>-1</sup> were detected. The former could be assigned to the monodentate carbonate and the latter was the bands of ion carbonate [8]. But for t-ZrO<sub>2</sub>, no formate species but bicarbonate and bi-dentate carbonate with bands at 1647, 1614 and 1292 cm<sup>-1</sup> formed as CO adsorption at 623 K.

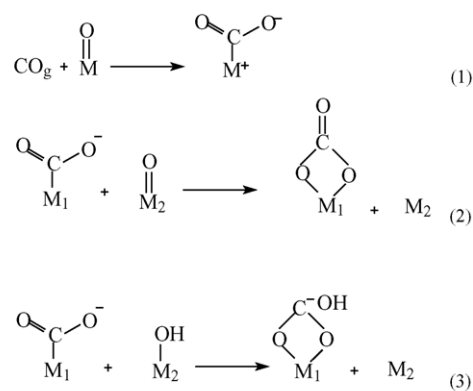
The mechanism of formate formation through CO reaction with surface hydroxyls could be formulated as Scheme 1. Hydroxyl and O<sup>2-</sup>, which had different families on zirconia polymorphs, played an important role in the formation of intermediate species. CO reacted with hydroxyl to form the formate species and consumed a certain hydroxyl group at high temperature, showing negative peaks in the hydroxyl region (Fig. 5A). On the other hand, bicarbonate and carbonate were formed when CO contacted with surface O<sup>2-</sup>. In the case of t-ZrO<sub>2</sub>, the surface basicity was strong and the surface oxygen ions were abundant. The adsorption CO might quickly react with O<sup>2-</sup> to form the carboxylate and further to bicarbonate and carbonate by reacting with hydroxyl or O<sup>2-</sup> (see Scheme 2). This might be responsible for the complicated carbonate as well as the absence of formate species on t-ZrO<sub>2</sub>.

### 3.3. CO + H<sub>2</sub> adsorption

Fig. 6 showed the DRIFT spectra of CO/H<sub>2</sub> adsorbed on three zirconia polymorphs at 623 K. Similar to pure



Scheme 1. Proposed reaction scheme for formate formation on zirconia surface.



(M<sub>1</sub> and M<sub>2</sub> were Zr<sup>4+</sup> and/or Zr<sup>3+</sup>, respectively)

Scheme 2. Proposed reaction scheme for carbonate and bicarbonate formation on zirconia surface.

CO adsorption, formate species with bands at 2968, 2880, 1563, 1390 and 1360 cm<sup>-1</sup> was detected (see Fig. 6A). In addition, a weak band located at 3077 cm<sup>-1</sup>, attributable to gas methane species [23], was observed. Hydrogen could be homolytically or heterolytically dissociated to form hydroxyl or adsorbed hydrogen on zirconia [24], which facilitated the hydrogenation formate to methoxide and then to methane. On the other hand, according to the thermodynamics, the

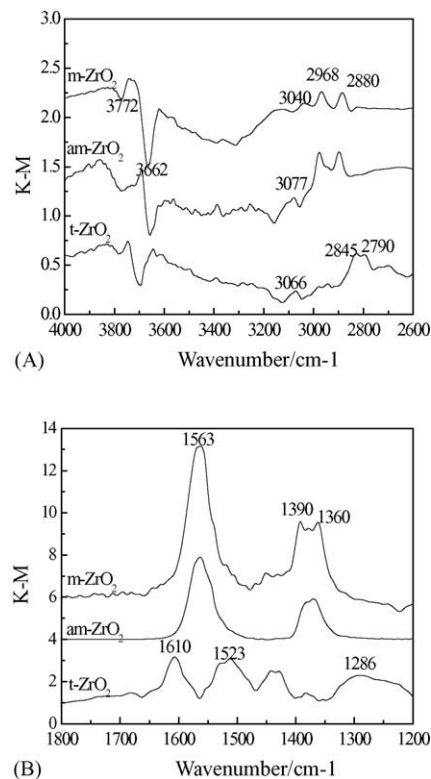


Fig. 6. Difference DRIFT spectra of CO/H<sub>2</sub> adsorption on three zirconia polymorphs. Section A: hydroxyl and νC-H region (4000–2600 cm<sup>-1</sup>); section B: surface intermediates region (1800–1200 cm<sup>-1</sup>).

formation of methane was 9 times higher than that of methanol at ambient pressure under syngas atmosphere [25]. Hence, methane was formed from CO hydrogenation on am-ZrO<sub>2</sub> at 623 K. Similar phenomena were observed in the case of CO/H<sub>2</sub> adsorption onto m-ZrO<sub>2</sub> (with the methane band lowering to 3040 cm<sup>-1</sup>), and formate species also could be detected at 623 K. Compared to pure CO adsorption on m-ZrO<sub>2</sub>, the carbonate and ion carbonate species were absent due to the presence of hydrogen.

In the case of CO/H<sub>2</sub> adsorption on t-ZrO<sub>2</sub>, no formate was produced even in the presence of hydrogen. Compared to pure CO adsorption, the bidentate carbonate species located at 1647 cm<sup>-1</sup> disappeared while the bicarbonate was also present, which might be the contribution of hydrogenation. Other bands at 1523 and 1286 cm<sup>-1</sup>, ascribable to monodentate carbonate species, were also detected. Onishi and co-workers [26,27] concluded that the reaction of hydroxyl groups with CO gave rise to bicarbonate, and the methoxide species also could be obtained by hydrogenation of bicarbonate with the formaldehyde as intermediate species. Methane species with band at 3066 cm<sup>-1</sup> was formed on t-ZrO<sub>2</sub> though no formate was appeared (see Fig. 6). But formaldehyde species with bands at 2845 and 2790 cm<sup>-1</sup> was detected. A comparison of different species formation on zirconia polymorphs established the conclusion that the methane formation on am-ZrO<sub>2</sub> and m-ZrO<sub>2</sub> came from the hydrogenation of formate but it came from bicarbonate hydrogenation on t-ZrO<sub>2</sub>.

As shown above, CO reacted with surface hydroxyl to form formate and bicarbonate species and then caused hydroxyl to decrease and appear two negative peaks at 3772 and 3660 cm<sup>-1</sup>. The negative peak of tri-bridged hydroxyl was larger than that of terminal one (see Fig. 6A), but it was not confirmed that the tri-bridged hydroxyl was more active than that of terminal one because the intensity of tri-bridged hydroxyl on zirconia polymorphs was stronger than that of the terminal one (see Fig. 1).

#### 4. Conclusions

Different zirconia polymorphs possessed varied surface hydroxyl groups and acid–base properties. Bi-bridged hydroxyl only existed on tetragonal zirconia and amorphous zirconia showed obvious H-band hydroxyl while two type of tri-bridged hydroxyl appeared on monoclinic zirconia. These differences effected surface acidity and basicity: amorphous zirconia had strong Lewis acid sites and monoclinic zirconia had strong Brønsted acid sites, but for tetragonal zirconia, the basicity was predominant. Subsequently, surface properties greatly influenced the formation of surface intermediates as CO or CO/H<sub>2</sub> adsorption. Formate was formed on amorphous and monoclinic zirconia while no formate but bicarbonate

and carbonate were present on tetragonal zirconia, whether hydrogen introduce or not. Though methane was formed on three zirconia polymorphs, the intermediate species was different on three zirconia polygraphs.

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