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Journal of Catalysis 227 (2004) 556–560

JOURNAL OF CATALYSIS

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Reseach Note

In situ DRIFT-mass spectrometry study of the ethanol steam-reforming reaction over carbonyl-derived Co/ZnO catalysts

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Received 21 May 2004; revised 27 July 2004; accepted 17 August 2004

Abstract

The ethanol steam-reforming reaction was studied by in situ diffuse reflectance infrared Fourier transform spectroscopy and on-line mass spectrometry over ZnO and a Co/ZnO catalyst prepared from impregnation of $Co_2(CO)_8$. Acetaldehyde is the primary product. The presence of cobalt favors the reforming of acetaldehyde, via the C–C scission of bidentate acetate species. Dimethyl ketone is produced as a by-product on ZnO. The roles of ZnO support and cobalt are discussed on the basis of surface species and their subsequent evolution.

Keywords: Ethanol steam reforming; Acetaldehyde; Surface acetate; Cobalt catalyst

1. Introduction

The ethanol steam reforming,

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2, \qquad (1)$$

is a process which is gaining consideration in hydrogen production for fuel cell applications [1,2]. Several active phases have been proposed to serve as catalyst for this reaction [3–5]. However, no attention has been paid to determining the surface species under reaction conditions, and this can yield insight into the pathway of the process.

In light of mainly catalytic results, over ZnO-supported cobalt catalysts prepared by a coprecipitation method, a first step of ethanol dehydrogenation to acetaldehyde and then the steam reforming of acetaldehyde through surface acetate species has been proposed [6]. On the other hand, we have previously reported a comparative study of supported cobalt catalysts prepared from impregnation of $Co_2(CO)_8$ over several oxides which were used in the steam reforming of ethanol without ulterior calcination or reduction steps. Only 1% wt/wt cobalt loading was used, and significant differences in the behavior of catalysts were shown, depending on the support used. This in turn determined the evolution of cobalt species under reaction conditions. The study showed ZnO-supported catalyst to yield the best catalytic performance [7,8]. To afford better insight into the different pathways concerning the ethanol steam reforming, the present contribution reports on an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) study under reaction conditions with on-line analysis of evolved products by mass spectrometry (MS) carried out over the ZnO-supported catalyst. Results were compared with those corresponding to ZnO used as support.

2. Methods

The ZnO-supported cobalt catalyst (Co/ZnO) with ca. 1.0% by weight metal loading was prepared by impregnation from a *n*-hexane $Co_2(CO)_8$ solution on ZnO support ($100\ m^2\ g^{-1}$) as previously described [7].

Infrared study was performed with a Nicolet Magna-IR 750 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector using a Spectra Tech Inc. catalytic DRIFT chamber. The outlet of the DRIFT chamber was

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2004.08.024

connected on-line through a capillary tube held at 423 K to a Balzers instrument equipped with a quadrupole mass spectrometer. Several mass values were selected and previously calibrated in the apparatus in order to monitor the evolution of different products (hydrogen, carbon oxides, C1–C4 hydrocarbons, ethanol, acetaldehyde, dimethyl ketone, acetic acid, and crotonaldehyde). A feed of gaseous $C_2H_5OH + H_2O$ (HPLC grade) was introduced into the DRIFT chamber by bubbling helium (20 ml min^{-1}) through a thermostated saturator maintained at 308 K. The partial pressure of C_2H_5OH was 0.4 kPa and the H_2O/C_2H_5OH molar ratio was ca. 13. The samples were transferred into the DRIFT chamber under inert atmosphere.

Catalytic tests were performed in a U-shaped quartz continuous-flow reactor with on-line analysis of products by gas chromatography as described elsewhere [6].

3. Results and discussion

3.1. Adsorption of $C_2H_5OH + H_2O$

The initial spectrum of the Co/ZnO sample recorded at 298 K under He flow showed bands in the υ(CO) (carbonyl) region at 2067, 1999, 1950, and 1933 cm^{-1} which can be assigned to $[Co(CO)_4]^-$ species with a C_{2v} symmetry [9,10]. The introduction of the reaction mixture at 298 K produced a displacement of the carbonylic bands to lower wavenumbers and a progressive diminution of their intensities. Moreover, an absorption centered at 1886 cm^{-1} appeared, which may be assigned to tetrahedral $[Co(CO)_4]^-$ deposited on the surface [9]. However, all bands due to cobalt carbonylic species disappeared after prolonged exposure to the reaction mixture at 298 K.

Simultaneously, the interaction of the reaction mixture with the surface of Co/ZnO progressively produced bands characteristic of ethoxy species at 2973 ($\upsilon_{as}(CH_3)$), 2928 ($\upsilon_{as}(CH_2)$), 2900 ($\upsilon_s(CH_3)$), 2874 ($\upsilon_s(CH_2)$), 1381 ($\delta_s(CH_3)$), 1100 ($\upsilon(CO_{mono})$), and 1057 ($\upsilon(CO_{bi})$) cm^{-1} [11,12]. Moreover, a well-defined band at 1275 cm^{-1} and smaller absorptions at 2755, 1348, 1148, and 972 cm^{-1} became progressively visible. These bands can be assigned to a η^2-acetaldehyde species: υ(CH), 2755; $\delta(CH_3)$, 1348; υ(CO), 1275; υ(CC), 1148; and $\rho(CH_3)$, 972 cm^{-1}. η^2-Acetaldehyde species has been found to be formed after acetaldehyde adsorption over metallic surfaces such as Rh(111), Pd(111), or Ru(001) [13–15] as well as over metal-supported catalysts such as Co/CeO_2 or Pd/CeO_2 [16]. These species decompose at low temperature to carbon, hydrogen, and CO. In some cases the evolution of η^2-acetaldehyde species to acyl species before the decomposition pathway has been determined [14].

During the adsorption of the reaction mixture onto Co/ZnO, negative bands in the υ(OH) region located at 3620, 3640, 3670, and 3685 cm^{-1} were also generated. The first three bands are related to surface hydroxyl groups of ZnO [17], whereas that appearing at higher wavenumbers (3685 cm^{-1}) can be tentatively assigned to OH groups on Co(II) species like the CoO phase [18]. In agreement with this assignation, the interaction of the reaction mixture with the ZnO sample, which was used as support, produced bands due to surface ethoxy species and negative bands at 3620, 3640, and 3670 cm^{-1}. A similar behavior in the absence of water has been reported for the interaction of ethanol with hydroxyl groups of ZnO [19]. It can be concluded that the adsorption of the reactant mixture onto the Co/ZnO sample produced the disappearance of the initial carbonylic surface species and the formation of ethoxy species via the ethanol interaction with the OH surface groups of ZnO and CoO. The evolution of surface ethoxy species to η^2-acetaldehyde can be related to the presence of cobalt.

3.2. The ethanol steam-reforming reaction

The catalytic performance of Co/ZnO and ZnO samples in the ethanol steam-reforming reaction at 723 K, under total ethanol conversion, has already been reported [7,20]. When the reaction mixture comes into contact with Co/ZnO sample at increasing temperatures (573–723 K) the generation of small cobalt particles progressively takes place and the extension of the ethanol steam-reforming reaction increases [8]. For a better comparison of both samples, Table 1 shows their catalytic performances at ethanol conversion values lower than 100%. The presence of cobalt favors H_2 production. If the dehydrogenation of ethanol to acetaldehyde is assumed as the first step of the process, the reforming of acetaldehyde will be favored over Co/ZnO with respect to ZnO.

Table 1
Catalytic performance after 2 h of reaction under an $C_2H_5OH + H_2O +$ Ar stream ($C_2H_5OH{:}H_2O = 1{:}13$, $Ar/(C_2H_5OH + H_2O) = 5$, molar ratios) at atmospheric pressure and GHSV=5000 h^{-1}, 0.1 g of catalyst

Catalyst	T (K)	Conv. (%)	Product distribution[a] (%)						
			H_2	CO_2	CH_4	C_2H_4	C_3H_6	CH_3CHO	Me_2CO
ZnO	623	10.3	62.3	12.8	–	2.4	–	22.5	–
	673	87.9	61.0	21.8	0.1	1.9	0.1	5.9	9.2
Co/ZnO	623	17.9	66.3	15.1	–	2.4	–	15.2	1.0
	673	81.1	70.3	19.8	0.2	1.6	–	0.6	7.5

[a] Molar percentage, water not included.

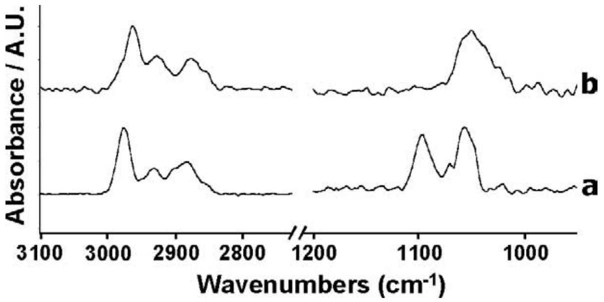

Fig. 1. DRIFT spectra in the υ(CH) and υ(C–O) regions under steam reforming of ethanol at 573 K: (a) over Co/ZnO, (b) over ZnO.

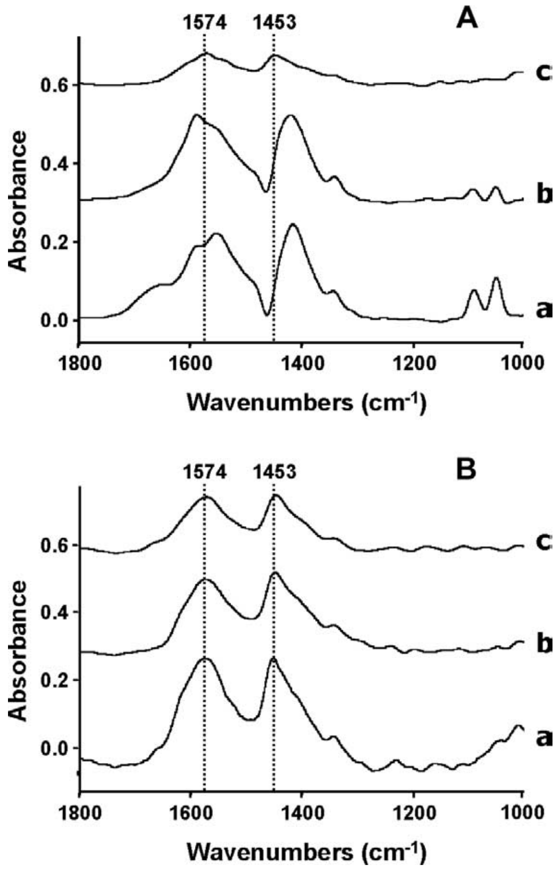

Fig. 2. DRIFT spectra corresponding to Co/ZnO (A) and ZnO (B): (a) after reaction at 673 K and quenching under He down to 298 K; (b) subsequent temperature-programmed desorption under He at 473 K; (c) subsequent temperature-programmed desorption under He at 673 K.

In separate experiments, the ethanol steam-reforming reaction was carried out over Co/ZnO and ZnO in the catalytic DRIFT chamber between 573 and 673 K. The samples were heated under He from 298 up to 573 K, and then the reaction mixture of $C_2H_5OH + H_2O$ was added to the He flow. In both cases, the evolution of H_2, CO_2, methane, acetaldehyde, and dimethyl ketone was detected by mass spectrometry. Under these conditions, DRIFT experiments enabled identification of surface ethoxy species. Characteristic υ(C–O) bands corresponding to mono- ($\upsilon(\mathrm{CO}) = 1096\ \mathrm{cm}^{-1}$) and bidentate ($\upsilon(\mathrm{CO}) = 1055\ \mathrm{cm}^{-1}$) ethoxy species were observed for Co/ZnO sample (Fig. 1, spectrum a). Over ZnO, mainly bidentate ethoxy surface species was identified, $\upsilon(\mathrm{CO}) = 1050\ \mathrm{cm}^{-1}$ (Fig. 1, spectrum b). In both cases, besides the bands corresponding to ethoxy species, other weak bands in the zone 1600–1400 cm^{-1} appeared. However, their unambiguous assignation was not possible. Furthermore, a band at 1713 cm^{-1} in the spectrum corresponding to Co/ZnO sample could indicate the presence of physisorbed acetaldehyde.

An increase of the reaction temperature up to 673 K and subsequent quenching under He down to room temperature yielded relevant IR information. The spectrum corresponding to Co/ZnO (Fig. 2A, spectrum a) clearly showed υ(C–O) bands due to mono- and bidentate ethoxy species and bands at 1660, 1591, 1555, 1450–1380, and 1343 cm^{-1}. The presence of two different surface acetate species can be proposed, $\upsilon_{\mathrm{assym}}$(COO) at 1591 and 1555 cm^{-1}, respectively, υ_{sym}(COO) at 1450–1380 cm^{-1}, and $\delta(\mathrm{CH_3})$ at 1343 cm^{-1}. The separation between $\upsilon_{\mathrm{assym}}$(COO) and υ_{sym}(COO) bands indicated that the configuration of these surface acetate species was probably bidentate or bridge [21,22]. The band at 1660 cm^{-1} was ascribed to an acetyl species. An acetyl species characterized by an IR band at 1685 cm^{-1} has been reported on cobalt-doped CeO_2 after acetaldehyde adsorption and heating at 335 K [16].

For ZnO, broad bands with maxima at 1574 and 1453 cm^{-1} were also assigned to surface acetate species, probably bidentate or bridge, too (Fig. 2B, spectrum a).

After reaction at 673 K and quenching under He at 298 K, a temperature-programmed desorption experiment (TPD) was carried out. Fig. 3 shows the evolution of mass profiles as a function of temperature for both catalysts Co/ZnO (Fig. 3A) and ZnO (Fig. 3B). In both cases, hydrogen, carbon dioxide, acetaldehyde, methane, dimethyl ketone, and ethanol showed a maximum at ca. 473 K. This indicates that ZnO could be responsible for the generation of these products at this temperature.

Simultaneously, a comparison of the IR spectrum of Co/ZnO recorded after heating at 473 K (Fig. 2A, spectrum b) and that obtained after quenching (Fig. 2A, spectrum a) showed a decrease in the intensity of the bands corresponding to the ethoxy species, in accordance with the results of MS measurements. At ca. 473 K, some of the ethoxy species could desorb as ethanol. However, these species can easily evolve to acetaldehyde through α-H elimination over ZnO [23].

Different studies of acetaldehyde decomposition over ZnO have indicated the reaction of aldehyde with lattice oxygen via a nucleophilic attack of lattice oxygen at the carbonyl carbon of the aldehyde, followed either by hydride elimination to produce the corresponding surface carboxylate or by alkyl elimination to produce formate and stable surface alkyl species. At lower temperatures, alkyl elimination is favored (260 K), while at higher temperatures (600–750 K) the decomposition of carboxylates to atomic adsorbed carbon, water, and CO_2 was observed [24].

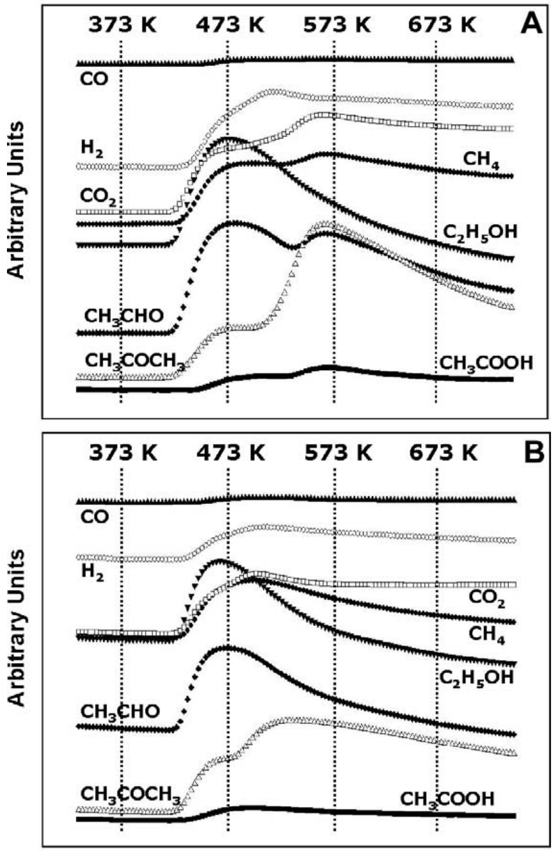

Fig. 3. Products evolved as determined by mass spectrometry during TPD experiments of surface species obtained after ethanol steam reforming at 673 K and subsequent quenching under He at 298 K: (A) Co/ZnO catalyst, (B) ZnO.

Regarding the formation of dimethyl ketone, it can be obtained from acetaldehyde by two different routes. The first pathway is via the acetaldehyde oxidation to acetate and then the coupling of two carboxylates to form dimethyl ketone and CO_2. The second pathway is through the reaction of an adsorbed acetyl group with an adsorbed ($–CH_3$) group [16].

As stated above, the decomposition of acetaldehyde by alkyl elimination is favored at low temperatures over ZnO, and this process could be the main one responsible for the CO_2, CH_4, and H_2 maxima in the TPD experiment at 473 K. Dimethyl ketone can also be formed over ZnO at this temperature from acetaldehyde by oxidation and aldolization reactions.

Significant differences between TPD profiles corresponding to Co/ZnO and ZnO are evidenced at higher temperatures. Co/ZnO exhibited a second maximum at ca. 563 K for the evolution of CO_2, methane, acetaldehyde, and dimethyl ketone. The comparison of IR spectra after TPD experiment at 473 and 673 K for this catalyst showed the almost total disappearance of bands due to acetate species (see Fig. 2A). Thus, it can be proposed that the products evolved come from surface bidentate acetate species, which easily decompose over Co/ZnO by C–C scission. The presence of surface –OH may favor this pathway, giving the final products CO_2, CH_4, and H_2. H_2 did not show a maximum at this temperature, probably due to its consumption in the hydrogenation of acetate species to give acetaldehyde under the TPD experimental conditions. On the other hand, dimethyl ketone and CO_2 may be formed from the coupling of two acetate species.

Contrasting with the behavior of Co/ZnO, the TPD experiment corresponding to ZnO did not show a second maximum for the evolution of different products at ca. 573 K, and the IR spectrum indicated a lower diminution of the intensity of bands due to surface acetate species over ZnO when the sample was heated from 473 to 673 K (see Fig. 2B). Over ZnO the decomposition of surface acetate species via C–C scission was not favored, and probably only some of these species evolved to dimethyl ketone and CO_2 via an aldolization reaction. According to this proposition, for Co/ZnO catalyst, after the TPD experiment at 673 K (Fig. 2A, spectrum c) only residual bands in the region 1600–1400 cm^{-1} remained, and these corresponded to acetate species over ZnO (compare spectrum c of Fig. 2A with spectra in Fig. 2B).

Taking into account all these results, it is possible to propose an initial interaction of ethanol with the –OH groups of ZnO and CoO to form ethoxy species, which could evolve to acetaldehyde. This proposition accords with catalytic studies carried out with ZnO-supported cobalt catalysts, which have pointed out that acetaldehyde is an intermediate product in the steam reforming of ethanol over these systems [6]. In a second step, acetaldehyde may either evolve over ZnO through alkyl elimination or form a bidentate acetate species, which in the presence of cobalt may favor the C–C scission, producing CO_2, CH_4, and H_2 in the presence of water. Although it was not possible to evidence by IR the presence of surface formate species, their presence cannot be ruled out because their characteristic bands may be masked by the intense bands of acetate and ethoxy species.

Quantitative analysis of products under reaction conditions (see Table 1) indicated that the main process under these conditions was the ethanol steam reforming,

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2,$$

and not the decomposition of ethanol and ulterior water gas shift reaction:

$$C_2H_5OH \rightarrow CO + CH_4 + H_2,$$

$$CO + H_2O \rightarrow CO_2 + H_2.$$

In both cases, and before the C–C scission, the dehydrogenation of ethanol to acetaldehyde takes place. Resulting surface species would be reformed to CO_2 and H_2 [25]. However, carbon deposition on catalysts after reaction indicated that some (CH_x) species did not evolve to CH_4 or CO_2, but remained on the surface and generated carbonaceous residues [7].

4. Conclusions

Over Co/ZnO the ethanol steam-reforming reaction takes place via the initial dehydrogenation of ethanol to acetaldehyde, which can evolve via the C–C scission or by producing bidentate (or bridge) acetate surface species. Ethoxy, acetate, and acyl surface species are present under ethanol steam-reforming conditions. The C–C scission of acetate species is related to the H_2 production in the steam-reforming reaction of ethanol, which is favored when cobalt is present. On the other hand, dimethyl ketone production is related to ZnO used as support.

Acknowledgments

We thank MCYT (MAT 2002-01739) and CIRIT (2001 SGR-00052) for financial support. J. Ll. is grateful to MCYT for a Ramon y Cajal research program and DURSI (Generalitat de Catalunya).

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