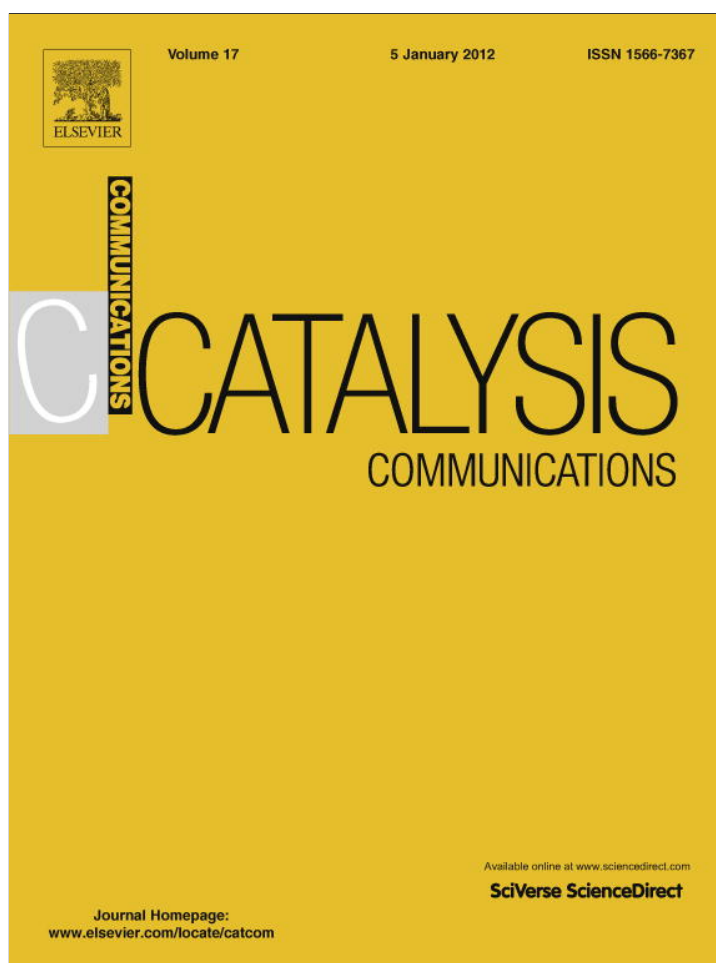


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Short Communication

Enhanced C₂ oxygenate synthesis by CO hydrogenation over Rh-based catalyst supported on a novel SiO₂

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ABSTRACT

A novel SiO₂ synthesized by the Stöber method was studied as the support for Rh–Mn–Li catalyst, and better performance for C₂ oxygenate synthesis via CO hydrogenation was achieved compared with the counterpart using commercial SiO₂ as the support. The investigation based on the catalytic performance and characterizations of the catalysts suggests that the hydroxyl–metal interaction over the catalyst supported on SiO₂ prepared by the Stöber method results in a change in the CO adsorption on Rh particles, which promotes the CO dissociation and CO insertion, leading to higher CO conversion and C₂ oxygenate selectivity.

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1. Introduction

The synthesis of ethanol and other C₂ oxygenates (e.g. acetaldehyde and acetic acid) from syngas derived from coal or biomass, has attracted much attention in recent years because it can reduce the global dependence on petroleum [1–3]. Rh-based catalysts have been known to be the most efficient ones in this process due to their unique CO adsorption behavior [4–6]. Since single Rh component is restricted by its poor catalytic performance, numerous efforts have been focused on enhancing the yield of C₂ oxygenates of Rh with additives and supports [5–10], and SiO₂-supported Rh-based catalyst exhibits the most practical application due to its good performance for C₂ oxygenate synthesis [11].

Considerable researches heretofore have been performed to investigate the promoting effects of additives [6–9], less attention has been focused on the SiO₂ support, although the catalytic activity is also correlated intimately with the chemical nature of SiO₂. For example, treatment of silica support with nC₁–C₅ alcohols resulted in an enhancement of the space time yield (STY) of C₂ oxygenates by 10–30% depending on the specific alcohol [10]. Basu et al. [12] reported that Rh⁺ could be formed by an oxidation of the Rh⁰ clusters by the surface OH groups on SiO₂. These results show that the surface properties of SiO₂, in particular the surface hydroxyls, would affect the chemical state of Rh, which finally affect the performance of the Rh/SiO₂-based catalyst. The Stöber method, which can prepare monodispersed spherical silica with abundant surface hydroxyls on it, is invented by W. Stöber in 1968 [13]. Combined with the above discussion, it is proposed that the SiO₂ prepared

by the Stöber method is potentially suitable to the support materials for the Rh-based catalysts for the synthesis of C₂ oxygenates.

In this paper, a novel SiO₂ prepared by the Stöber method was studied as the support for Rh-based catalyst, and its catalytic performance for C₂ oxygenate synthesis was compared with the counterpart using commercial SiO₂ as the support. With regard to the additives, it has been reported that Mn and Li can improve the CO conversion and oxygenate selectivity, respectively [14,15]. In order to compare the catalytic performance of the catalysts more clearly, here we took a known recipe of Rh–Mn–Li [16], as a part of screening for catalysts with a high activity and C₂ oxygenate selectivity. Meanwhile, the correlation between the surface hydroxyl groups on SiO₂ and catalytic performance of the Rh/SiO₂-based catalyst was discussed for the first time.

2. Experimental

2.1. Catalyst preparation

SiO₂, which was denoted as SiO₂(SM), was prepared by the Stöber method as reported in Ref. [17]. In a typical synthesis, the mixture solution of 21 mL tetraethylorthosilicate (TEOS) and 50 mL anhydrous ethanol was added slowly into the mixed solution of 76 mL NH₃·H₂O (26 vol.%) and 200 mL anhydrous ethanol. Then, this synthesis solution was aged for 4 h and separated centrifugally at 7000 r.p.m. Finally, the collected product was washed with de-ionized water and dried at 70 °C for 12 h. The commercial SiO₂ from the Qingdao Ocean Desiccant Co, PR China, was denoted as SiO₂(CM). In order to remove the surface impurities, SiO₂(CM) was boiled in de-ionized water for 24 h and dried

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at 90 °C for 12 h. Before being used, they were calcined in static air at 550 °C for 4 h.

Aqueous solutions of RhCl₃ hydrate (Rh ~36 wt.%), Mn(NO₃)₂·6H₂O and Li₂CO₃ were co-impregnated on the SiO₂ mentioned above, dried overnight at 120 °C and calcined for 4 h at 350 °C (Rh loading was 1.5 wt.% and the weight ratio of Rh:Mn:Li = 1.5:1.5:0.07). The obtained catalysts were denoted as RML/SiO₂(SM) and RML/SiO₂(CM), respectively.

2.2. Catalyst testing

CO hydrogenation was performed in a fixed-bed micro-reactor with length ~350 mm and internal diameter ~5 mm. The catalyst (0.3 g) was diluted with inert α-alumina (1.2 g) to avoid channeling and hot spots. Prior to reaction, the catalyst was reduced in a stream of 10% H₂/N₂ at 400 °C for 2 h under atmospheric pressure. Then, the reactor was cooled to 300 °C and the reaction started at a gas hourly space velocity (GHSV) of 10,000 mL/(g·h) and pressure of 3 MPa. The feed gas contained 60% H₂, 30% CO and 10% N₂. All post-reactor lines and valves were heated to 150 °C to prevent product condensation [18]. The products were analyzed on-line (Agilent GC 6820) using a HP-PLOT/Q column (30 m, 0.32 mm ID) with detection with an FID (flame ionization detector) and a TDX-01 column with a TCD (thermal conductivity detector). Conversion and selectivity values were calculated by mass-balance method and the steady-state values were quoted as the average of four different analyses. The CO conversion was calculated based on the fraction of CO that formed carbon-containing products according to: %Conversion = $(\sum n_i M_i / M_{CO}) \cdot 100\%$, where n_i is the number of carbon atoms in product i , M_i is the percentage of product i detected, and M_{CO} is the percentage of carbon monoxide in the syngas feed. The selectivity of a certain product was calculated based on carbon efficiency using the formula $n_i C_i / \sum n_i C_i$, where n_i and C_i are the carbon number and molar concentration of the i th product, respectively.

2.3. Catalyst characterization

The morphologies of supports were observed by a Hitachi S-4000 scanning electron microscope (SEM). The BET surface area of sample was obtained by N₂ adsorption at -196 °C on a Micromeritics ASAP 2020 apparatus. The X-ray powder diffraction (XRD) spectra of samples were obtained on a Rigaku D/MAX-III A X-ray diffractometer with CuKα ($\lambda = 0.15418$ nm).

The CO adsorption was studied on a Nicolet 6700 FT-IR spectrometer equipped with a DRIFT (diffuse reflectance infrared Fourier transform) cell. The sample in the cell was pretreated in 10% H₂/N₂ at 400 °C for 2 h, and then the temperature was dropped to 30 °C. After the cell was outgassed in vacuum to $<10^{-3}$ Pa, the background was scanned. After CO was introduced for 30 min ($p_{CO} = 8.0 \times 10^3$ Pa), the IR absorption spectrum of CO adsorbed on the catalyst was recorded. The spectral resolution was 4 cm⁻¹ and the scan times were 32.

The CO temperature-programmed desorption (TPD) was carried out in a quartz microreactor. The catalyst (100 mg) was reduced in

situ in 10% H₂/N₂ at 400 °C for 2 h, and then was held at 400 °C for another 30 min in He flow before being cooled down to room temperature. The next step was CO adsorption in the pure CO flow for 30 min, and then the gas was swept again with He for 3 h. Subsequently, the catalyst was heated at a rate of 10 °C/min in He flow. The desorbed species were monitored by the quadruple mass spectrometer (QMS, Balzers OmniStar 200).

3. Results and discussion

3.1. Catalytic performance

Table 1 shows the performances of the two catalysts for CO hydrogenation. It can be seen that the RML/SiO₂(SM) exhibits an excellent CO conversion of 13.7%, more than twice that on RML/SiO₂(CM). The turnover frequency (TOF) of CO conversion over RML/SiO₂(SM) is also higher than that over RML/SiO₂(CM) catalyst. A higher C₂ oxygenate selectivity along with a lower CO₂ and CH₄ selectivity is obtained on RML/SiO₂(SM) compared with the RML/SiO₂(CM). Moreover, it is noteworthy that the STY of C₂ oxygenates increases remarkably from 72.6 g/(kg·h) of RML/SiO₂(CM) to 198.5 g/(kg·h) of RML/SiO₂(SM).

3.2. Textural and structural properties

The SEM micrographs of supports in Fig. 1 show that the particles of SiO₂(SM) are monodispersed sphericals with a mean size of 500 nm, but SiO₂(CM) has no definite morphology. The BET surface areas of SiO₂(SM) and SiO₂(CM) are 11.3 m²/g and 328.9 m²/g, respectively (Table 2). The surface area of the former is similar to that of silica prepared with the Stöber method by Szekeres and Hsu et al. [17,19]. For the pore distribution, SiO₂(SM) and SiO₂(CM) have a similar pore in the range of 7–9 nm. After supporting metal components, the surface areas and pore volume of catalysts were decreased, likely due to pore plugging by the metal components. In the XRD patterns of the prepared catalysts (not shown), no discernable peaks related to any crystalline phase can be observed, indicating that the metal particles are highly dispersed.

Based on the above results, it is found that the catalyst of RML/SiO₂(SM) with smaller BET surface area gave higher activity and selectivity of C₂ oxygenates. Most researchers reported that a support with a high surface area generally favors the dispersion of metal species, further improves the catalytic conversion of syngas to oxygenates [20]. However, different opinions were also proposed by other authors. For example, Fan et al. [21] found that the high surface area is not the decisive factor for the dispersion of metal species in the carbon-supported Rh-based catalyst. In fact, combination of the nanochannels and graphitic structure plays an important role in promoting CO hydrogenation in these Rh-based catalysts. Moreover, Chen et al. [22] studied the effect of SBA-15 on Rh/Mn-supported catalysts on CO hydrogenation, and found that the catalytic performance has clear dependence on the different chemical properties of SBA-15 modified by different promoters rather than

Table 1
Catalytic performance of the Rh–Mn–Li/SiO₂ catalysts for CO hydrogenation.

Catalyst	Conversion of CO (%)	TOF ^a (s ⁻¹)	Selectivities of products ^b (%)						STY of C ₂ oxy (g/(kg·h))
			CO ₂	CH ₄	MeOH	C ₂ oxy ^c	C ₂ ⁺ HC ^d	Other oxy ^e	
RML/SiO ₂ (CM)	6.5	0.030	17.5	11.8	5.9	33.8	27.5	3.5	72.6
RML/SiO ₂ (SM)	13.7	0.137	5.5	10.1	3.5	46.7	32.0	2.2	198.5

Reaction conditions: 300 °C, 3 MPa, GHSV = 10,000 mL/(g·h), V(H₂)/V(CO) = 2, data taken after 15 h when steady state reached. Experimental error: ± 5%.

^a TOF based on CO conversion and H₂ chemisorption.

^b Based on carbon efficiency, carbon selectivity = $n_i C_i / \sum n_i C_i$.

^c C₂ Oxy denotes oxygenates containing two carbon atoms.

^d C₂⁺ HC denotes hydrocarbons containing two and more carbon atoms.

^e Other Oxy denotes oxygenates containing more than two carbon atoms.

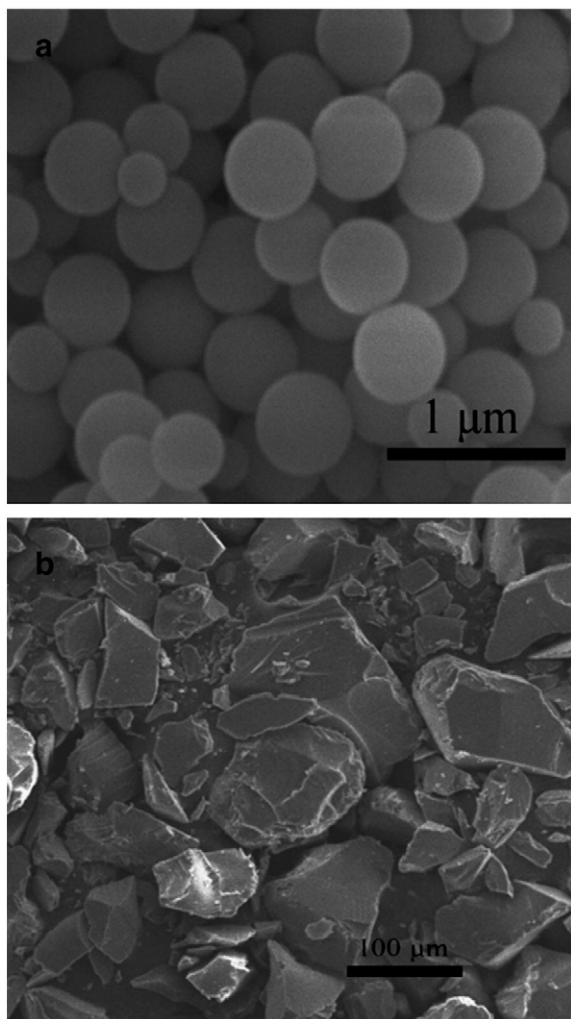


Fig. 1. The SEM micrographs of (a) SiO₂(SM) and (b) SiO₂(CM).

the surface areas. In this work, we also infer that there are some other chemical properties rather than surface area of silica, such as the role of hydroxyl on silica mentioned by many researchers [12,23–25], which affect the catalytic performance of catalysts supported on SiO₂.

The IR spectra of SiO₂ and the corresponding catalysts in N₂ atmosphere at 300 °C are presented in Fig. 2. In these IR spectra, the band at 3735 cm⁻¹ arises from the absorption of isolated OH groups; the absorption peaks at 3670–3630 cm⁻¹ are assigned to the weakly H-bonded OH groups; and the bands at 3500–2750 cm⁻¹ originate from the absorption of H₂O and strongly H-bonded OH groups [19]. It can be seen from Fig. 2 that more amount of weakly H-bonded hydroxyl groups cover on the surface of SiO₂(SM), whereas the concentration of hydroxyls on the surface of SiO₂(CM) is lower. After supporting metal components, it is obvious that the amount of the weakly H-bonded hydroxyl decreases and the amount of isolated hydroxyls increases over SiO₂(SM), which might point to a metal–

Table 2

BET surface areas (S_{BET}), pore volume (V_p) and pore diameter (D_p) of SiO₂ supports and the corresponding catalysts.

Sample	S_{BET} (m ² /g)	V_p (cm ³ /g)	D_p (nm)
SiO ₂ (SM)	11.3	0.021	7.9
RML/SiO ₂ (SM)	10.9	0.021	6.7
SiO ₂ (CM)	328.9	0.877	9.2
RML/SiO ₂ (CM)	321.4	0.828	9.0

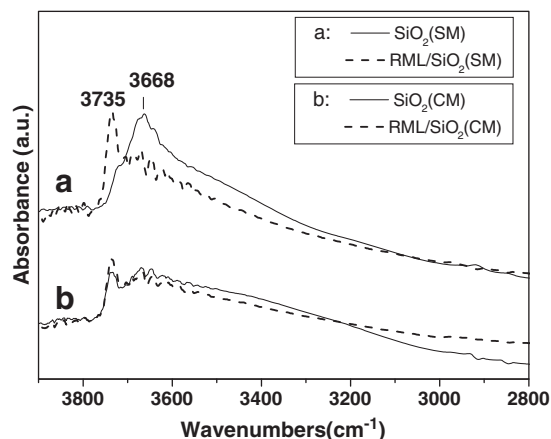


Fig. 2. FT-IR spectra of (a) SiO₂(SM) (straight) and RML/SiO₂(SM) (dash), (b) SiO₂(CM) (straight) and RML/SiO₂(CM) (dash) in N₂ flow at 300 °C.

hydroxyl interaction. In fact, a similar interaction between the silver species and H-bonded hydroxyls has also been observed by Qu et al. [26]. However, for the RML/SiO₂(CM) catalyst, there is nearly no change in an absorption intensity of hydroxyl groups, implying a little metal–hydroxyl interaction. By combining the activities of the catalysts and the above discussion, it can be inferred that the perfect catalytic performance of RML/SiO₂(SM) catalyst might be related to the hydroxyl–metal interaction.

3.3. The chemical state of rhodium

The FT-IR spectra of in situ reduced catalysts after CO adsorption at 30 °C for 30 min are given in Fig. 3. The IR spectrum is mainly composed by a band at ~2067 cm⁻¹ and a doublet at ~2100 and ~2030 cm⁻¹, which can be attributed to linear adsorbed CO [CO(l)] and dicarbonyl Rh⁺(CO)₂ [CO(gdc)], respectively [10]. Meanwhile, a weak broad peak at ~1800 cm⁻¹ is assigned to bridge-bonded CO [CO(b)] [10]. It is widely accepted that the CO(l) is formed on the Rh⁰ sites, and CO(gdc) species is on the Rh⁺ sites which are highly dispersed [10]. It can be seen that, both the peak intensity of adsorbed CO and the peak area ratio of CO(gdc)/CO(l) (Rh⁺/Rh⁰) on RML/SiO₂(SM) are lower than that on RML/SiO₂(CM), implying that the hydrophobicity of the silica surface is favorable for increasing Rh dispersion [27]. Since both Rh⁰ and Rh⁺ sites are active for CO adsorption, while H₂ is known to be adsorbed dissociatively on Rh⁰ sites [28], it can be inferred that a higher relative surface coverage of H* and CO* ($\theta_{\text{H}}/\theta_{\text{CO}}$) would be obtained on RML/SiO₂(SM) catalyst under the reaction conditions due to its lower ratio of Rh⁺/Rh⁰ than

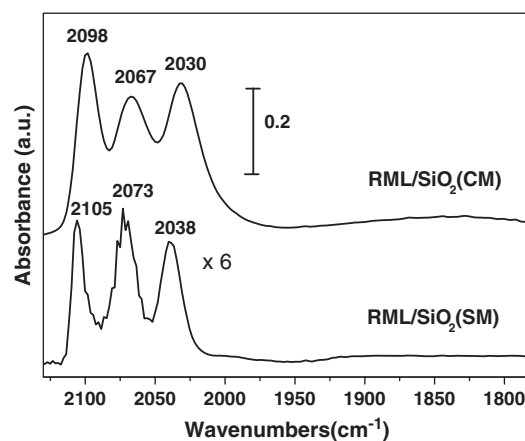


Fig. 3. FT-IR spectra of CO chemisorbed on catalysts at 30 °C for 30 min.

that on RML/SiO₂(CM). As suggested that hydrogen-assisted CO dissociation is the rate-limiting step for CO hydrogenation [4,29], it is more likely that the increased θ_{H} may assist CO dissociation on RML/SiO₂(SM), leading to increased CO conversion.

Moreover, the position of adsorbed CO on RML/SiO₂(SM) shifts significantly to higher frequency compared with that on RML/SiO₂(CM), suggesting that the CO–Rh bond strength was weakened by the hydroxyl–metal interaction. In fact, Basu et al. [12] also considered that hydroxyl groups on oxide supports can be involved in changes in the oxidation state of the metal, which can affect the CO adsorption. Since the C₂ oxygenates should be formed by the reaction route-insertion of CO into a metal–CH_x bond [4], it is likely that the weakened CO–Rh bond on RML/SiO₂(SM) is favorable for increased CO insertion, and accordingly the increase of C₂ oxygenate selectivity.

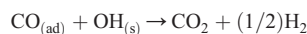
3.4. TPD analysis

The desorption profiles of CO ($m/z = 28$), CO₂ ($m/z = 44$) and H₂ ($m/z = 2$) in CO-TPD of RML/SiO₂ are showed in Fig. 4. In the desorption profiles of CO (Fig. 4a), the desorption peaks at ~105 and 160 °C correspond to CO(l) and CO(gdc) species, respectively; while the peak at >250 °C may be assigned to the desorption of CO(b) species or other forms [30]. It is obvious that the desorption amount of adsorbed CO is consistent with the IR results (Fig. 3).

The results in Fig. 4b show that, the CO₂ desorption is observed at ~160 °C on the catalysts, and this temperature of desorption peak is the same as that of CO(gdc) species. It is suggested that CO(gdc) was desorbed in two different modes: (a) an associative desorption, (b) after being dissociated these species further react to form CO₂. Based on the amount of CO₂ desorption at ~160 °C, it is obvious that the CO(gdc) species on RML/SiO₂(SM) was dissociated more easily

than that on RML/SiO₂(CM), which may also be due to the change in the CO–Rh bond strength.

When the desorption temperature exceeds 250 °C, the desorption peaks of CO₂ became broader and complicated, and a H₂ desorption peak was observed, which is similar to the Rh catalysts supported on Al₂O₃ and TiO₂ [31,32] where the CO₂ is suggested to be formed by the reaction of surface hydroxyls with the strongly adsorbed CO species:



The high-temperature CO₂ peak on RML/SiO₂(CM) is located at 400 °C, which is 80 °C higher than that on RML/SiO₂(SM), suggesting that the strongly adsorbed CO is less reactive on RML/SiO₂(CM) due to the weak metal–hydroxyl interaction. This is in good agreement with lower activity on RML/SiO₂(CM) for CO hydrogenation (Table 1) [32].

4. Conclusions

The Rh–Mn–Li catalyst supported on a novel support of SiO₂(SM), exhibits higher activity and C₂ oxygenate selectivity for CO hydrogenation compared with that on SiO₂(AM). The excellent performance of Rh–Mn–Li/SiO₂(SM) should be attributed to the special interaction between Rh particles and weakly H-bonded hydroxyls over SiO₂(SM), which finally affects the CO adsorption behavior on Rh.

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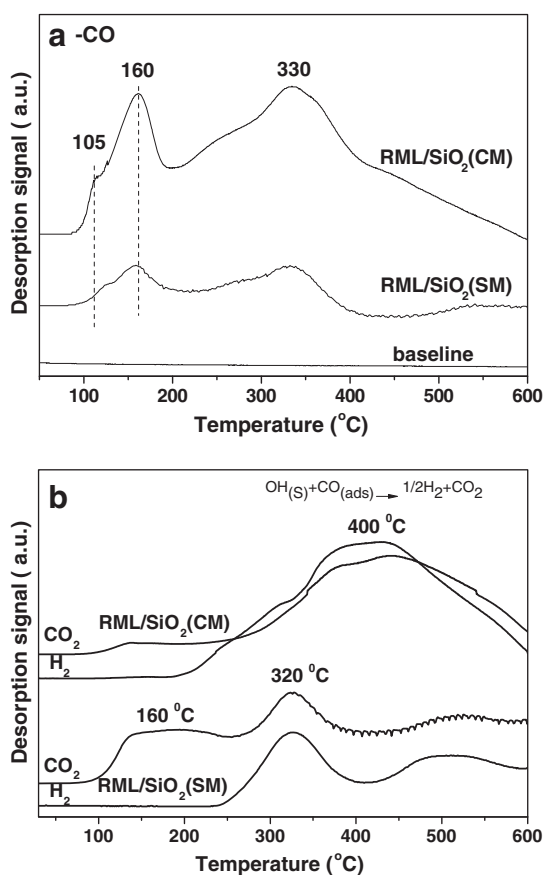


Fig. 4. Desorption profiles of (a) CO ($m/z = 28$), (b) CO₂ ($m/z = 44$) and H₂ ($m/z = 2$) in CO-TPD of catalysts, after CO adsorption at room temperature.

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