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Effect of alkali metals on the performance of CoCu/TiO₂ catalysts for CO₂ hydrogenation to long-chain hydrocarbons

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ABSTRACT

CoCu/TiO₂ catalysts promoted using alkali metals (Li, Na, K, Rb, and Cs) were prepared by the homogeneous deposition-precipitation method followed by the incipient wetness impregnation method. The influences of the alkali metals on the physicochemical properties of the CoCu/TiO₂ catalysts and the catalytic performance for CO₂ hydrogenation to long-chain hydrocarbons (C₅₊) were investigated in this work. According to the characterization of the catalysts based on X-ray photoelectron spectroscopy, X-ray diffraction, CO₂ temperature-programmed desorption (TPD), and H₂-TPD, the introduction of alkali metals could increase the CO₂ adsorption and decrease the H₂ chemisorption, which could suppress the formation of CH₄, enhance the production of C₅₊, and decrease the hydrogenation activity. Among all the promoters, the Na-modified CoCu/TiO₂ catalyst provided the maximum C₅₊ yield of 5.4%, with a CO₂ conversion of 18.4% and C₅₊ selectivity of 42.1%, because it showed the strongest basicity and a slight decrease in the amount of H₂ desorption; it also exhibited excellent catalytic stability of more than 200 h.

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1. Introduction

Carbon dioxide is one of the major components of the greenhouse gases emitted to the atmosphere from human utilization of coal, fossil fuels, and natural gas. The increasing concentration of CO₂ in the atmosphere has resulted in global warming and ocean acidification, which could eventually lead to natural disasters such as floods, hurricanes, and droughts, if

not addressed [1,2]. Stabilizing the concentration of CO₂ requires a decrease in emissions and the active removal of CO₂ from the atmosphere [3–6]. Therefore, CO₂ capture and utilization to convert the captured CO₂ into useful products is receiving increasing attention worldwide [7–13]. There are other successful examples of commercially available technologies for CO₂ conversion to methanol or methane [14–18]. Another promising investigation is CO₂ hydrogenation to hydrocarbon

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fuels, especially for long-chain hydrocarbons (C_{5+}) via the CO_2 Fischer-Tropsch (CO_2 -FT) reaction [19–22].

Hydrogenation of CO_2 to hydrocarbons consists of two reactions in series: the reverse water gas shift (RWGS) reaction (Eq. (1)) and Fischer-Tropsch synthesis (FTS) (Eq. (2)) [23]. CO_2 hydrogenation produces more water, which is a deactivation agent for iron-based FTS catalysts, than conventional FTS. In addition, Co-based catalysts are preferred over Fe-based catalysts in FTS to synthesize C_{5+} because of their ability for chain growth and stability [24–27]. Moreover, the degree of hydrogenation of the surface-adsorbed intermediates in the CO_2 -FT reaction is higher than that for synthesis gas conversions because of the slower adsorption rate of CO_2 , resulting in a lower CO_2 conversion and easier formation of a large fraction of CH_4 [28]. Consequently, the main challenge is to develop catalysts with high activity and selectivity toward C_{5+} .

Since the 1980s, CoCu-based catalysts have attracted much attention for CO hydrogenation to synthesize higher alcohols, where the copper species act as a CO insertion site and the cobalt species function as a CO dissociation site [29–31]. In our previous work, the CO_2 hydrogenation products were mainly hydrocarbons (especially CH_4) and CO over modified Co/TiO₂ and Cu/TiO₂ catalysts, respectively). Therefore, when CoCu/TiO₂ catalysts were employed for the CO_2 hydrogenation reaction, the CO_2 molecule was initially reduced to CO by H_2 via RWGS on Cu sites, followed by the subsequent hydrogenation of CO to hydrocarbons via FTS on Co sites [20]. Alkali metals, especially K and Na, are usually used as chemical promoters for the CO_2 hydrogenation reaction [32–36], which were reported to increase the FTS activity and C_{5+} selectivity [33,37]. It has been shown that alkali metals can suppress CH_4 production and increase the selectivity for higher hydrocarbons. The reasons for this phenomenon may be that the incorporation of alkali metals can cause a charge transfer from the alkali metals to the surface of the catalysts, thereby inhibiting H_2 adsorption but enhancing CO_2 chemisorption and dissociation [20]. Therefore, the investigation into the influence of alkali metals on the CO_2 -FT reaction is of vital importance.

In the present work, a series of CoCu/TiO₂ catalysts promoted by various alkali metals were prepared by the deposition-precipitation method followed by the incipient wetness impregnation method. The oxide-support interactions, roles of alkali metals in the reduction of the catalyst, and phase evolution of the catalysts after reduction were fully characterized by multiple techniques. Moreover, the effect of the alkali metals on the catalytic performance for CO_2 hydrogenation was studied.

2. Experimental

2.1. Catalyst preparation

The cobalt-copper-based catalysts were prepared by the deposition-precipitation method using TiO₂ (TiO₂ P25 Evonik Industry, 80% anatase and 20% rutile) as a support. First, a certain amount of a $Co(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ aque-

ous solution (the total metal loadings of Co and Cu were 30 wt%, and the Co/Cu molar ratio was 1) and the required amount of aqueous ammonia were added to a four-necked flask. Then, TiO₂ was added with vigorous stirring for 0.5 h. Subsequently, the mixture was kept at 90 °C under stirring for 12 h to evaporate ammonia with N_2 bubbling. When the precipitation was complete, the CoCu/TiO₂ samples were filtered, dried at 100 °C overnight, and calcined at 350 °C for 4 h. The individual Co/TiO₂ and Cu/TiO₂ catalysts were also synthesized following the same method. Finally, a certain amount of the alkali metals (the alkali metal loading was about 2.5 wt%) was incorporated into the as-prepared CoCu/TiO₂ samples via an incipient wetness impregnation method; the obtained catalyst is denoted as x-CoCu/TiO₂ (x = Li, Na, K, Rb, or Cs).

2.2. Catalytic performance tests

The performance of the x-CoCu/TiO₂ catalysts for the CO_2 hydrogenation reaction was studied in a fixed bed reactor, and 1.5 g of the catalyst and the same volume of quartz sand (both in 40–60 mesh) were packed into the reactor. Prior to the reaction, the catalyst was reduced at 350 °C for 8 h in pure hydrogen. After reduction, the activities of the catalysts in the CO_2 hydrogenation process were determined under reaction conditions of 250 °C, 5.0 MPa, $H_2/CO_2/N_2 = 73/24/3$ (vol%), and weight hourly space velocity (WHSV) = 3000 mL·g_{cat}⁻¹·h⁻¹. The gaseous products were analyzed on-line after passing through a cold trap by gas chromatography (GC 2014C, Shimadzu). H_2 , N_2 , CO, CH_4 , and CO_2 were analyzed through a TDX carbon molecular sieve column equipped with a thermal conductivity detector (TCD), while the hydrocarbons were analyzed through a modified alumina-packed column equipped with a hydrogen flame ionization detector. The aqueous products gathered from the cold trap were analyzed off-line using Porapak-Q columns equipped with a TCD. The conversion and selectivity were calculated based on the carbon balance.

2.3. Catalyst characterization

The textural properties of the catalysts, such as the specific surface area, pore volume, and pore size distribution, were measured by a standard Brunauer-Emmett-Teller (BET) procedure using N_2 adsorption at -196 °C on an automatic physisorption analyzer (ASAP 2420, Micromeritics). All the samples were degassed at 200 °C for 10 h prior to adsorption. The pore size distribution curves were collected from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model.

The compositions of the catalysts were determined by sequential X-ray fluorescence (XRF) spectroscopy using a LAB CENTER XRF-1800 spectrometer (Shimadzu, Japan).

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD spectrometer equipped with Al $K\alpha$ radiation (150 W, $h\nu = 1486.6$ eV) under ultrahigh vacuum (10^{-7} bar). The binding energies (E_b) were calibrated internally by adventitious carbon deposit C (1s) with $E_b = 284.8$ eV.

The crystal structures of the cobalt-copper-based catalysts were measured using an X-ray diffractometer (XRD, Ultima IV, Rigaku) using Cu $K\alpha$ (0.154 nm) radiation of 40 mA and 40 kV from 5°–90° and a scanning step of 0.0667°. Transmission electron microscopy (TEM) micrographs of the catalysts were obtained using a JEOL JEM 2000FX microscope operating at 200 kV. Prior to the measurements, all samples were dispersed in ethanol and dropped on a nickel microgrid covered by a holey-carbon film.

The H_2 temperature-programmed reduction (H_2 -TPR) experiments were carried out in a U-tube quartz reactor using a Micromeritics ChemiSorb 2920 instrument equipped with a TCD. The samples were pretreated with an Ar gas flow at 120 °C for 2 h and cooled to 50 °C. Once the TCD signal was stable, the gas flow was switched to a 5% (v/v) H_2 /Ar stream, and the temperature was then raised from 50 to 500 °C at the rate of 5 °C·min⁻¹.

The basicity of the catalysts was studied by CO_2 temperature-programmed desorption (CO_2 -TPD) experiments on the same apparatus as that employed for H_2 -TPR. All the samples were reduced *in situ* under a H_2 atmosphere at 350 °C for 1.5 h. After cooling to 50 °C, the samples were flushed with Ar for 0.5 h, after which all the samples were exposed to pure CO_2 for 1 h and then flushed with an Ar flow to remove the physically adsorbed molecules. Finally, desorption was performed by raising the temperature from 50 to 750 °C at the rate of 5 °C·min⁻¹, and the CO_2 desorption profiles were obtained using a mass spectrometer.

The H_2 -TPD experiments were performed using the same apparatus as that for H_2 -TPR. All the samples were pretreated at 350 °C for 2 h in a 5% (v/v) H_2 /Ar flow. After cooling to 50 °C, the samples were saturated with pure H_2 for 1 h and then flushed with Ar to remove the physically adsorbed molecules. Then, the TPD experiments were performed at the heating rate of 5 °C·min⁻¹ at 50–600 °C under an Ar atmosphere. The H_2 signal was monitored by a TCD detector.

Thermal gravimetric (TG) analysis was performed on a thermogravimetric analyzer (STA449F3, NETZSCH) under Ar to determine the weight loss for the modified catalysts. The samples were heated in Ar flow at the rate of 5 °C·min⁻¹ to 1000 °C, and the flow rate was maintained at 50 mL·min⁻¹.

3. Results and discussion

3.1. Characterization

The metal content in the catalyst was derived from the XRF measurements and is listed in Table 1. As can be seen from Table 1, the content of alkali metals and the Co/Cu molar ratio were in close agreement with the nominal compositions used for preparing the catalysts, indicating that there were no obvious metal losses. Additionally, the added alkali metals may exist in the form of carbonates under the reduction conditions at 350 °C due to the much higher decomposition temperature of carbonates, which can be seen from the TG curves of those samples (Fig. S1). The $LiNO_3$ promoter may decompose into an oxide during the reduction process (350 °C), while lithium ox-

Table 1

Textural properties of the CoCu/TiO₂ and x-CoCu/TiO₂ catalysts.

Sample	Alkali metal loading ^a (wt%)	Co/Cu molar ratio ^a	S_{BET} (m ² ·g ⁻¹)	V_{BJH} (cm ³ ·g ⁻¹)	D_{pore} (nm)
CoCu/TiO ₂	—	1.00	37.3	0.26	35.2
Li-CoCu/TiO ₂	—	0.99	28.3	0.24	34.2
Na-CoCu/TiO ₂	2.76	1.01	37.2	0.22	24.1
K-CoCu/TiO ₂	2.51	1.00	33.9	0.23	27.5
Rb-CoCu/TiO ₂	2.38	0.99	36.9	0.25	25.5
Cs-CoCu/TiO ₂	2.32	0.99	29.1	0.25	34.7

^a Determined by XRF.

ide would be easily converted to carbonate under a CO_2 atmosphere because the Gibbs free energy for this reaction is negative.

The N_2 adsorption-desorption isotherms and pore size distributions of the CoCu/TiO₂ catalysts with various alkali metals are shown in Fig. 1. At relative pressures (p/p_0) of 0.8–1.0, all the samples show roughly type-I hysteresis loop, which implies that they have more regular cylindrical channels [38]. As shown in the inset in Fig. 1, a very broad pore distribution with a maximum at ~35 nm was observed for all the samples, and it decreased slightly with the increase in the atomic number of the alkali metal. Table 1 presents the BET surface areas, pore volumes, and average pore sizes of the catalysts; for the catalysts promoted by Li, K, and Cs alkali metals, the BET surface areas were slightly less than that of the pure CoCu/TiO₂ catalyst. There is no obvious difference in the pore volume of the promoted catalysts.

The XRD patterns of the calcined, reduced, and spent catalysts are shown in Fig. 2(a), (b), and (c). As can be seen from Fig. 2(a), the diffraction peaks at 35.5°, 38.7°, 48.6°, 61.4°, and 68.0° are assigned to the CuO phase (JCPDS card No.80-1916), and the peaks at 31.3°, 36.8°, and 65.2° are attributed to Co_3O_4 (JCPDS card No.74-2120); the Co and Cu particle sizes were calculated using the Scherrer equation and are listed in Table S1. Among all the samples, there are no diffraction peaks associated with the alkali metals, which is probably due to their low concentrations and good dispersion. Additionally, the intensi-

Fig. 1. N_2 adsorption-desorption isotherms and BJH pore size distributions (inset) of the CoCu/TiO₂ and x-CoCu/TiO₂ catalysts.

Fig. 2. XRD patterns of calcined (a), reduced (b), and spent (c) catalysts.

ties of the characteristic peaks of all six catalysts are similar, indicating that the alkali metals have no obvious effect on the crystallite structure of the CoCu-based catalyst. For the reduced catalysts, the diffraction peaks are observed at 43.3° , 50.4° , and 74.1° , which correspond to (111), (200), and (220) of metallic Cu⁰ (JCPDS card No.85-1326), respectively (Fig. 2(b)), and both the Co and Cu particle sizes changed slightly with the introduction of different alkali metals. The intensity of the characteristic peaks related to metallic Cu⁰ and Co⁰ for the spent catalysts (Fig. 2(c)) increased slightly compared with the corresponding fresh catalysts, suggesting that the particles aggregated moderately and the catalysts possessed a high stability.

The calcined, reduced, and used catalysts of representative Na-CoCu/TiO₂ were characterized by TEM and high-resolution TEM (HRTEM) (Fig. 3). As can be seen in the TEM images, the

oxide particles were highly dispersed and the size changed slightly after the reduction and reaction, indicating that the dispersion and stabilization of the active components could be enhanced by this synthesis method (Fig. 3(a)–(c)). As shown in Fig. 3(e), metallic Co and Cu formed after reduction, and the metal phase could also be observed after the reaction (Fig. 3(f)), which is consistent with the XRD characterization. Moreover, the Cu and Co species were separately dispersed on the TiO₂ support, even after the reduction and reaction.

XPS characterization was used to analyze the surface evolution of the catalysts; the results are listed in Table 2, and the spectra of Co 2p_{3/2}, Cu 2p_{3/2}, and Ti 2p_{3/2} are shown in Fig. S2. From Table 2, we can see that the binding energies of Co 2p_{3/2} and Ti 2p_{3/2} shift to lower values with the modification of alkali metals. The XPS results indicate that the electron density

Fig. 3. TEM and HRTEM images of the calcined (a, d), reduced (b, e), and spent (c, f) Na-CoCu/TiO₂ catalysts.

Table 2XPS results for the CoCu/TiO₂ and x-CoCu/TiO₂ catalysts after reduction.

Sample	Binding energy (eV)			Relative surface concentration of metal (at%)				Co/Cu atomic ratio
	Co 2p _{3/2}	Cu 2p _{3/2}	Ti 2p _{3/2}	Co	Cu	Ti	Alkali metal	
CoCu/TiO ₂	780.7	932.7	458.5	24.6	16.4	59.0	—	1.5
Li-CoCu/TiO ₂	780.4	932.8	458.3	11.2	10.1	52.8	25.9	1.1
Na-CoCu/TiO ₂	780.4	932.7	458.3	14.6	8.3	50.7	26.4	1.7
K-CoCu/TiO ₂	780.2	932.9	458.1	17.8	12.7	50.9	18.6	1.4
Rb-CoCu/TiO ₂	780.0	932.1	458.1	17.6	10.9	58.6	12.9	1.6
Cs-CoCu/TiO ₂	780.1	932.1	458.2	17.6	14.5	55.1	12.8	1.2

around both the Co and Ti atoms increased with the modification of alkali metals [33]. As for the Rb- and Cs-modified catalysts, the E_b of Cu 2p_{3/2} was much lower than that of the other samples, probably because the chemical environments of the Cu ions was affected by the promoters [35]. Similar results were obtained by other researchers; for example, the sodium promoter is assumed to donate an electron to the surface of iron, as evidenced by the reduced work function of iron [39,40]. The surface compositions of the catalysts as determined by XPS analysis are also listed in Table 2. Compared with the bulk compositions listed in Table 1, the surface modifiers (Li, Na, K, Rb, and Cs) accumulated preferentially on the surface (more than five to ten times that for the bulk composition), which can enhance the dispersion of the active components. In addition, the surface content of the alkalis decreased gradually with the increase in atomic number. This can be ascribed to the fact that the atomic weights of Li and Na are much lower than that of Cs, and thus more Li and Na atoms were introduced into the catalysts for the same weight loading of alkali metals. The Co/Cu surface ratios after reduction were also calculated and compared with the results detected by XRF (Table 1). The Co/Cu ratio in the bulk is about 1; however, the Co/Cu surface ratio in the catalysts changed depending on the properties of the alkali metal promoters (Table 2). After the reduction, the Co/Cu surface ratio increased in the order Li < Cs < K < Rb < Na, and these values were higher than 1, indicating that the surface was enriched by Co.

The reduction behaviors of the catalysts were investigated using H₂-TPR. As shown in Fig. 4, all the reduction profiles con-

sisted of several overlapping peaks, which were the characteristic peaks of the step-reduction of the metal oxide. As mentioned in our previous work, the lower temperature reduction peaks corresponded to the reduction of CuO to metallic Cu, and the peaks at higher temperatures were attributed to the reduction of Co₃O₄ to CoO and CoO to metallic Co [20]. The reduction of the CoCu/TiO₂ and modified catalysts occurred at a much lower temperature than that for the Co/TiO₂ and K-Co/TiO₂ catalysts (Fig. S3). With the introduction of the copper species, the interactions between CuO and Co₃O₄ weakened the metal oxide chemical bonds, which could increase the reducibility of Co₃O₄ [41,42]. It is noteworthy that the reduction of catalysts was restricted and the reduction peaks shifted towards higher temperatures with the addition of alkali metals (Fig. 4 and Fig. S3). However, the maximum temperature of these reduction peaks was dependent on the alkalis. The highest reduction temperature occurred for the Rb-CoCu/TiO₂ catalyst, while the Na- and K-promoted catalysts shifted to a slightly higher temperature than that for the pure CoCu/TiO₂ catalyst. The reduction temperature peak increased in the order Na < K < Rb, and then decreased on the Cs promoter. For the catalyst with the Li promoter, both Co₃O₄ and CuO reduction were restrained, especially for the Cu²⁺ species, and thus the reduction peaks of those species overlapped to exhibit only one peak. In fact, the total amounts of hydrogen consumption were similar for all catalysts, indicating that all catalysts could be completely reduced. These results clearly indicated that the addition of the alkali metal inhibited the reduction of the catalysts. It might be due to the inhibiting effect of the alkali metals on the adsorption of H₂ [37].

The information on the surface basicity could be obtained

Fig. 4. H₂-TPR profiles of various catalysts after calcination. **Fig. 5.** CO₂-TPD profiles of various catalysts after reduction.

from the CO₂-TPD profiles of the pre-reduced catalysts; as exhibited in Fig. 5; there is a high and broad peak at around 150 °C in all the TPD profiles, which corresponds to the desorption of weakly adsorbed CO₂ in the bulk phase. With the introduction of alkali metals, especially for the K-CoCu/TiO₂ and Na-CoCu/TiO₂ catalysts, peaks at higher temperatures were observed, which corresponded to the desorption of CO₂ that interacted strongly with the surface basic sites. Moreover, Na-CoCu/TiO₂ exhibited the strongest basicity among all samples, which suggested that the alkali metals had a critical role in the surface basicity of the CoCu/TiO₂ catalyst.

Fig. 6 shows the H₂-TPD profiles of various catalysts. The peaks at around 150 °C correspond to the combinative desorption of atomic hydrogen on the surface of metallic Cu or Co sites [43]. The desorption temperature shifted to a slightly lower temperature with the increase in the atomic number of the alkalis [44]. In addition, the area of the desorption peak, which corresponds to the amount of H₂ desorption, for the alkali-metal-promoted catalysts (except for Li) was lower than that for pure CoCu/TiO₂. The remarkable decrease in the amount of H₂ desorption could be observed over the K-, Rb-, and Cs-modified CoCu/TiO₂ catalysts. These results indicate that the alkali metals donated electrons to the metal species, which resulted in a decrease in the number of electrons from hydrogen adsorption; this is consistent with the XPS results.

3.2. Catalytic performance

The catalytic performances of the alkali-metal-promoted catalysts were investigated to study the effect of the alkali promoters under the given reaction conditions. For comparison, the pure CoCu/TiO₂ catalyst was tested under the same reaction conditions. The catalytic activities and hydrocarbon selectivities are listed in Table 3. The products are mainly CO and hydrocarbons, and the selectivity of the oxy-compound is not listed because it was less than 0.5% when the reaction temperature was higher than 230 °C for the CoCu/TiO₂ and Na-CoCu/TiO₂ catalysts (Table S2). The cobalt catalyst was normally used in FTS applications for its higher chain growth probabilities [23,32]. However, when the feed gas was changed to CO₂ and H₂, the main product over the pure CoCu/TiO₂ catalyst was CH₄. The RWGS reactivity was very low, and the CO selectivity was only 1% for the CoCu/TiO₂ catalyst, as can be seen in Table 3. Therefore, it reacted as a methanation catalyst rather than as an FT catalyst under the reaction conditions.

Table 3

Catalytic performance for CO₂ hydrogenation over the x-CoCu/TiO₂ catalysts.

Sample	CO ₂ conversion (%)	CO selectivity (%)	Hydrocarbon distribution (%)			C ₅₊ yield ^a (%)
			CH ₄	C ₂ –C ₄	C ₅₊	
CoCu/TiO ₂	23.1	1.3	89.5	5.6	4.9	1.1
Li-CoCu/TiO ₂	38.2	1.1	87.1	10.3	2.7	1.0
Na-CoCu/TiO ₂	18.4	30.2	26.1	31.8	42.1	5.4
K-CoCu/TiO ₂	10.1	58.7	42.0	37.7	20.3	0.8
Rb-CoCu/TiO ₂	8.4	17.0	58.8	24.4	16.8	1.2
Cs-CoCu/TiO ₂	13.4	5.6	72.5	18.0	9.5	1.2

Reaction conditions: $p = 5.0$ MPa, $T = 250$ °C, WHSV = 3000 mL·g_{cat}⁻¹·h⁻¹, H₂/CO₂/N₂ = 73/24/3.

^a Yield C₅₊ = C_{CO2} × S_{total hydrocarbon} × S_{C5+}.

Fig. 6. H₂-TPD profiles of various catalysts after reduction.

According to the characterization results, the alkali metal promoters significantly modified the physical and chemical properties of the CoCu-based catalysts. The effect of the alkali metal promoters on the selectivity of products is mainly attributed to their different effects on the adsorption of CO₂ and H₂ [37]. As can be seen from Table 3, the CO₂ conversion dropped significantly with the addition of alkali metal promoters, except for Li, and it decreased slightly as the atomic number of the alkali metals increased, which can be explained by the CO₂/H₂-TPD results. The promotion of alkali metals increased CO₂ adsorption and suppressed H₂, which resulted in a low H₂/CO₂ ratio on the catalyst surface and consequently led to a low hydrogenation activity. Additionally, it was suggested that the CO₂ conversion was dependent on the amount of H₂ adsorbed [45,46]. The amount of adsorbed CO₂ was adequate, while the amount of atomic hydrogen was insufficient during the hydrogenation process under the operating conditions. In our case, with the decrease in H₂ adsorption, less atomic hydrogen was produced on the metal surface; as a result, less atomic hydrogen was available for both the adsorbed CO₂ species and formed CO intermediates, and thus the conversion of CO₂ decreased. However, for the Li-CoCu/TiO₂ catalyst, the CO₂ conversion increased and the selectivities of the products changed slightly compared with that for pure CoCu/TiO₂. From the viewpoint of the electron donor, the activity of the

Li-modified catalyst was low relative to its electronegativity, which is higher than that of the other alkali metals. From the viewpoint of the geometric effect, the activity of the Li-modified catalyst was higher than that of the others because the larger alkali metal ions may block the adsorption of reactants on the surface of the catalysts. The activities of the promoted catalysts should be determined by the two different factors of the geometric and electronic effect of alkali metals. Moreover, the polarization of the Li ion is the strongest among the alkali metals, which may result in an enrichment in the electron density at the interface between the alkali metal adlayer and Cu (Co) [47,48]. This characteristic of the Li ion was also related to the higher activity of the Li-promoted catalysts.

The formation of CH_4 was suppressed and the selectivity for C_{5+} increased remarkably with the introduction of alkali metals. As can be seen from the H_2 -TPD and CO_2 -TPD curves, the chemisorption of CO_2 and H_2 adsorption decreased with increasing atomic number for the alkali metals, which resulted in a decrease in the CO_2 conversion and the selectivity of C_{5+} . Typically, for the pure CoCu/TiO_2 catalyst, the CO_2 conversion was 23.1% and the selectivity of CH_4 was 89.5% in the overall hydrocarbon distribution; the C_{5+} selectivity and yield were only 4.9% and 1.1%, respectively. With the introduction of Na, K, and Rb promoters, the methane selectivity dropped and the C_{5+} selectivity increased remarkably, especially for Na- CoCu/TiO_2 . As mentioned above, Na- CoCu/TiO_2 exhibited the strongest basicity among all samples, and the amount of H_2 desorption decreased slightly with the introduction of Na. Additionally, Na- CoCu/TiO_2 possessed the largest amount of surface alkalis according to the XPS analysis. Therefore, a maximum C_{5+} yield of 5.4% with a CO_2 conversion of 18.4% and C_{5+} selectivity of 42.1% was obtained over Na- CoCu/TiO_2 . These results show that there is a correlation between the catalyst surface basicity and hydrocarbon distribution in the CO_2 hydrogenation process. The appropriate basicity of the CoCu/TiO_2 catalysts modified by alkali metals (such as Na and K) can effectively suppress the formation of CH_4 and increase the selectivity of C_{5+} . Furthermore, because of the different atomic weights of the alkali metals, the molar ratio of Co or Cu to the alkali metal changed when different alkali metals were added with a fixed-weight loading. As mentioned above, the atomic weights of Li and Na were much lower than that of Cs, and thus more Li and Na atoms were incorporated into the catalysts. For comparison, the Cs- CoCu/TiO_2 catalyst with a Cs/Co molar ratio similar to the Na/Co molar ratio for the Na- CoCu/TiO_2 sample was evaluated for CO_2 hydrogenation, and the results are listed in Table S3. When the Cs content increased from 2.5 to 10.5 wt%, although the C_{5+} selectivity increased slightly, the CO_2 conversion decreased and the CO selectivity increased markedly; thus, the C_{5+} yield decreased (Table S3). Similar results were also obtained by Telkar et al. [49]. They found that the product selectivity increased remarkably as the concentration of Cs increased from 0% to 1%; however, the product selectivity remained almost constant when the concentration of Cs was beyond 2%. Therefore, it can be concluded that the Na-promoted CoCu/TiO_2 catalyst exhibited the best performance for CO_2 hydrogenation to C_{5+} among all the alkali metal promoters.

Fig. 7. Catalytic performance over the Na- CoCu/TiO_2 catalyst as a function of the reaction time. Reaction conditions: $p = 5.0$ MPa, $T = 250$ °C, WHSV = $3000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, $\text{H}_2/\text{CO}_2/\text{N}_2 = 73/24/3$.

The long-term stability and activity of the catalysts are vital for CO_2 hydrogenation to hydrocarbons. The long-term catalytic performance for the representative Na- CoCu/TiO_2 catalyst was studied and is shown in Fig. 7. As can be seen, the C_{5+} selectivity dropped slightly during the first 24 h on stream and then remained relatively steady until the end of the duration test. Moreover, the CO_2 conversion and CO selectivity remained stable around 18% and 30% after 200 h, respectively, which indicates their potential for industrial applications.

4. Conclusions

A series of CoCu/TiO_2 catalysts promoted by various alkali metals (Li, Na, K, Rb, and Cs) were synthesized by the homogeneous deposition-precipitation method followed by the incipient wetness impregnation method, and the catalysts were evaluated for direct CO_2 hydrogenation to C_{5+} . The textural properties and crystal structures changed slightly with the incorporation of alkali metals, which normally reacted as electron promoters. The surface alkali metals accumulated preferentially on the surface and decreased gradually as the atomic number increased. In addition, the introduction of alkali metals enhanced the chemisorption of CO_2 and decreased H_2 adsorption, and then suppressed CH_4 formation and increased the selectivity of C_{5+} at the cost of CO_2 conversion, especially for the Na-modified CoCu/TiO_2 catalyst. Among all the alkali metal promoters, the Na-promoted CoCu/TiO_2 catalyst exhibited the best performance because of its strongest basicity and the slight decrease in the amount of H_2 desorption; it provided a maximum C_{5+} yield of 5.4% with a CO_2 conversion of 18.4% and C_{5+} selectivity of 42.1% with an excellent catalytic stability. The positive effects of the alkali promoters may guide the design and optimization of the direct hydrogenation of CO_2 to C_{5+} .

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Graphical Abstract

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Effect of alkali metals on the performance of CoCu/TiO₂ catalysts for CO₂ hydrogenation to long-chain hydrocarbons

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Among the alkali metals (Li, Na, K, Rb, and Cs), the Na-modified CoCu/TiO₂ catalyst exhibits the best performance because it shows the strongest basicity and reveals only a slight decrease in the amount of H₂ desorbed.

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碱金属助剂对 CoCu/TiO₂ 催化剂上二氧化碳加氢合成长链烃的影响

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摘要: 大气中 CO₂ 浓度增加导致的温室效应以及化石燃料的匮乏正日益受到世界范围的关注。由于 CO₂ 较强的惰性以及较高 C–C 偶联能垒, 迄今为止大部分研究都集中在 CO₂ 催化加氢制备各种 C1 化学品 (如 CH₄, CH₃OH, CO 等), 鲜有研究关注合成液态燃料 (C₅₊ 碳氢化合物)。目前, CO₂ 加氢直接合成烃类主要通过 CO₂ 基费托合成反应 (CO₂-FTS) 实现, 即先通过逆水煤气变换反应 (RWGS) 将 CO₂ 还原成 CO, 随后 CO 通过传统费托反应 (FTS) 加氢生成烃类化合物。在两种工业化 FTS 催化剂 (Fe 和 Co 基催化剂) 中, 钴基催化剂具有更高的反应活性和链增长能力, 以及较高的机械强度和稳定性。然而, 由于 CO₂ 的惰性, 造成催化剂表面物种的加氢程度更高, 使得甲烷更容易生成。因而, 高反应活性、高选择性催化剂的开发是实现该过程的关键。

本文采用沉积沉淀法制备了一系列双金属 CoCu/TiO₂ 催化剂, 再通过初湿浸渍法对其进行碱金属助剂 (Li, Na, K, Rb 和 Cs) 改性, 并用多种表征手段系统研究了碱金属助剂对催化剂物化性质及其催化 CO₂ 加氢制备长链烃反应的影响。结果表明, 碱金属的加入对催化剂织构性质影响不大, 它们在催化剂表面发生富集, 且富集程度随碱金属原子序数的增加而降低。另外, 碱金属的加入增强了 CO₂ 的吸附, 其中, Na 改性的 CoCu/TiO₂ 催化剂的碱性最强; 同时还降低了 H₂ 的脱附量, 尤以 K, Rb 和 Cs 改性的催化剂为甚。

在 250 °C, 5 MPa, 空速 3000 mL·g_{cat}⁻¹·h⁻¹ 和 H₂/CO₂ = 3 的反应条件下, 对不同碱金属助剂改性的催化剂进行评价。结果表明, 不加助剂的 CoCu/TiO₂ 催化剂上 CO₂ 转化率高达 23.1%, 但产物主要是 CH₄, 此时 CO₂ 在 Co 活性中心上直接发生甲烷化反应; 碱金属助剂的引入显著抑制了 CH₄ 的生成, 提高了长链烃的选择性, 但同时也降低了 CO₂ 转化率, 并且随着碱金属原子序数增大呈现先下降后上升的趋势, 表明合适的碱性强度可以更好地改性催化剂性能。其中, Na 助剂改性的 CoCu/TiO₂ 催化剂的碱性最强, 且 H₂ 的脱附量降低幅度较小, 因此, 该催化剂具有最高的 C₅₊ 烃类收率, 达到 5.4%; 同时 CO₂ 转化率为 18.4%, 烃类产物中 C₅₊ 烃类选择性为 42.1%。Na 助剂改性的 CoCu/TiO₂ 催化剂还展现了良好的催化稳定性, 反应 200 h 后, CO₂ 转化率和 C₅₊ 选择性分别保持 18% 和 40%。基于碱金属助剂对催化剂物化性质与反应性能的调变规律, 可进一步指导 CO₂ 加氢直接合成长链碳催化剂的设计与合成。

关键词: 二氧化碳加氢; 长链烃; 二氧化碳费托合成; 碱金属助剂; 钴-铜基催化剂

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