RSC Advances

PAPER

Cite this: RSC Adv., 2014, 4, 8930

Received 22nd May 2013 Accepted 17th January 2014

DOI: 10.1039/c3ra44485f www.rsc.org/advances

Introduction

Carbon dioxide capture, storage and utilization technologies (CCSU) are of great environmental importance in recent years because of the global greenhouse effect which is related to the rising level of CO₂ in the atmosphere.¹⁻⁴ Owing to the problem of depleting fossil resources, in particular coal and petroleum, the effort for developing sustainable energy technology in a variety of directions is receiving global attention during the past decade. From this point of view, various chemical approaches for converting CO₂, the most abundant carbon source available, into value-added products have been attempted,⁵⁻⁸ and catalytic hydrogenation of CO₂ to important chemical products is a potential approach.9

Many investigations have focused on the conversion of CO₂ into hydrocarbons.¹⁰⁻¹⁴ CO₂ hydrogenation over iron-based catalyst has been shown to proceed via a two-step process, with initial conversion of CO2 to CO via the reverse water gas shift reaction (RWGS) followed by CO hydrogenation into hydrocarbons as in Fischer-Tropsch synthesis reaction (FTS) as follows:15,16

to hydrocarbons†

higher CO₂ conversion to higher hydrocarbons.

$$CO + 2H_2 \rightarrow (-CH_2-) + H_2O FTS$$
(2)

$$CO + H_2O \rightarrow CO_2 + H_2 WGS$$
 (3)

The synthesis of value-added hydrocarbons from CO2 and CO hydrogenation reactions has something in common; the adsorption and activation of CO are of great importance. However, due to principle of microscopic reversibility, the intrinsic WGS and RWGS activity of iron-based catalyst should be taken into consideration. For instance, adsorption and activation of CO₂ behave differently in CO and CO₂ hydrogenation reactions, higher CO₂ conversion is facilitated in the former reaction, while more CO2 is obtained as main by-product in sole FTS reaction. In order to enhance the dissociative adsorption of CO2, alkali promoter can be added. Potassium is a significant promoter in CO2 hydrogenation reactions for enhancing the CO₂ adsorption and selectivity towards olefins, leading to a significant increase in CO₂ conversion.¹⁷ Riedel et al. reported a calculated equilibrium conversion of 72% at 573 K over a potassium-promoted iron catalyst, with direct hydrogenation of CO₂ merely playing a minor role.¹⁶ Moreover, Huo et al. demonstrated that potassium promoter (K_2O) could stabilize the high-index, more active facets, notably Fe (211) and change the relative rate of crystal growth in different directions to form small particles with a large percentage of more active facets.¹⁸ To improve the CO₂ hydrogenation performance, the addition of structural promoters or support into iron-based catalyst is beneficial to suppress the agglomeration of active

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Effect of SiO₂-coating of FeK/Al₂O₃ catalysts on

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their activity and selectivity for CO₂ hydrogenation

SiO₂-coated FeK/Al₂O₃ catalysts with different silica content were prepared and examined for the synthesis of hydrocarbons from CO₂ hydrogenation. It was found that SiO₂ coating affects both the activity for CO₂ conversion and the selectivity to higher hydrocarbons, depending on the loading level. The catalyst with 9 wt% SiO₂ coating showed both high CO₂ conversion (63%) and high selectivity toward C_{2+} hydrocarbons (74%), while further higher coating led to suppression of catalyst activity. The analytical characterization of SiO₂-coated catalysts confirmed the interactions of SiO₂-Fe and SiO₂-Al₂O₃, which largely reduced the metal-support interaction and decreased the reduction temperature of iron oxide. In addition, an

increase of adsorption capacity for CO was observed with desired SiO₂ coating. It is likely that SiO₂-

coating improved the catalyst hydrophobic property, thereby reducing the negative impact of water by-

product and facilitating the reverse water gas shift reaction and subsequent hydrogenation towards

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra44485f

phase and to improve the mechanical properties of the catalysts. Investigation of various modified iron catalysts showed alumina to be the best support for CO2 hydrogenation, followed by silica and titania.19 In spite of improvement of catalyst stability and stabilization of active sites of iron catalyst, it was found that the strong Fe-Al₂O₃ interaction inhibits the reduction and carbonization of iron catalyst, finally the FTS activity decreased.²⁰ Furthermore, although water has been identified as an effective agent in removing carbon deposits from metal surface, it is worth noting that the water generated during the reaction also suppresses the reaction rate of RWGS and FTS. It is postulated that an iron-based catalyst that facilitates the RWGS reaction can also catalyse the reverse reaction, thus inhibition of reaction rate by water could be more significant in CO2 hydrogenation than in FTS reaction using syngas, since the intermediate product CO could react with H2O for CO shift to CO_2 , resulting in a decrease of CO_2 conversion. For the methanol synthesis from CO₂ hydrogenation, Farsi and Jahanmiri proposed a water vapor-permselective alumina-silica composite membrane reactor to overcome the thermodynamic equilibrium limitations and increasing catalyst activity.21

Although many approaches have been reported to improve catalyst activity and C_2 + hydrocarbons selectivity, little is known about how surface silica coating affects the catalysts for CO_2 hydrogenation to hydrocarbons.²² In the present work, a series of SiO₂-coated FeK/Al₂O₃ catalysts with different SiO₂ contents were prepared and examined for CO₂ hydrogenation to hydrocarbons. Catalyst activity and product selectivities were evaluated in a fix-bed reactor. The catalysts were characterized by N₂ adsorption, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), H₂ temperature-programmed reduction (TPR), temperature-programmed desorption (TPD) of CO₂, H₂ and CO, and thermal gravimetric (TG) analysis.

Experimental

Preparation of Al₂O₃-supported catalysts

 γ -Al₂O₃ was used as the support material, which was obtained after calcining pseudo-boehmite in air at 773 K for 4 h. The FeK/Al₂O₃ catalyst was prepared by the incipient wetness impregnation method using aqueous solutions of iron and potassium nitrates (Fe(NO₃)₃·9H₂O and KNO₃), to obtain 15 wt % of Fe and 10 wt% of K loading, respectively. The fresh catalyst (denoted as 0Si) was obtained after drying at 393 K for 12 h followed by calcination in air at 773 K for 4 h to decompose iron and potassium nitrates, for which the heating rate was 2 K min⁻¹.

Preparation of the SiO₂-coated catalysts

A series of SiO₂-coated catalysts were prepared by impregnating the calcined 0Si catalyst with tetraethyl orthosilicate (TEOS) dissolved in cyclohexane at room temperature, dried at 393 K and then calcined at 773 K for 4 h. Calcination turned TEOS into SiO₂. SiO₂-coating contents of the 0Si catalyst were varied between 1 and 11 wt% and the corresponding samples were denoted as *x*Si (x = 1, 3, 5, 7, 9, 11).

CO₂ hydrogenation reaction

The catalytic hydrogenation of carbon dioxide was carried out in a pressurized fixed-bed flow reactor (inner diameter 8 mm) where a weighed 1 g catalyst (20–40 mesh) was loaded for each test. Prior to the reaction, the catalyst was pre-treated by reduction with pure H₂ at 673 K overnight. After the reduction, the feed gas was changed to the mixture of carbon dioxide and hydrogen under the reaction conditions of $n(H_2)/n(CO_2) = 3$ (molar ratio); P = 3 MPa; T = 673 K and the space velocity was 1800 ml g⁻¹ h⁻¹.

The products were analysed on-line by a gas chromatograph (FULI GC 97). Carbon monoxide, carbon dioxide and methane were analysed on a carbon molecular sieve column with a thermal conductivity detector (TCD) while methane and C_2 - C_8 hydrocarbons (C_2 +) were analysed with a flame ionization detector (FID) with a HayeSep Q column. Chromatograms of FID and TCD were correlated through methane and product selectivity was obtained based on carbon. The conversion percentage of CO₂ was based on the fraction of CO₂ that formed carbon-containing products according to:

$$CO_2 conversion(\%) = \frac{\sum n_i M_i}{M_{CO_2}} \times 100$$
(4)

where n_i is the number of carbon atoms in product *i*, M_i is the percentage of product *i* and M_{CO_2} is the percentage of carbon CO_2 in the mixed feed. The selectivity (*S*) to product *i*, is based on the total number of carbon atoms in the product and is therefore defined as:

$$S_i(\%) = \frac{n_i M_i}{\sum n_i M_i} \times 100 \tag{5}$$

Catalyst characterization

The textural properties of the samples were determined by N_2 adsorption on a Quantachrome AUTO-SORB-1-MP sorption analyser at liquid nitrogen temperature. Prior to the measurements, the samples were degassed at 623 K for 2 h. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method. The total pore volume was obtained from the amount of vapour adsorbed at a relative pressure (*P*/*P*₀) close to unity, where *P* and *P*₀ are the measured and equilibrium pressure respectively. The pore size distribution was evaluated using the Barrett–Joyner–Halenda (BJH) method.

XRD patterns of fresh and used catalysts were determined on a Rigaku D/Max 2400 diffractometer with Cu K α radiation ($\lambda =$ 1.5406 Å) source. The spectra were recorded from $2\theta = 5^{\circ}$ to 80° with 0.02° step size. The crystallite phases were identified by comparing the diffraction patterns with the data of the Joint Committee on Powder Diffraction Standards (JCPDS).

The FT-IR spectra were recorded with an EQUINOX55 (Bruker) Fourier transform infrared spectrometer by means of the KBr pellet technique. All spectra were taken in the range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. The spectra of all samples were presented by subtracting the background spectrum. The micro-IR imaging measurements were carried out with the OMNIC Picta software on a Nicolet iN 10 MX Infrared Microscope (Thermo Scientific).

 H_2 -TPR measurements were carried out with ChemBET *Pulsar* TPR/TPD equipment (Quantachrome, USA) to analyse the reducibility of the calcined catalysts. Prior to the reduction, the calcined sample (0.10 g) was placed in a quartz tube reactor in the interior of a controlled oven. The sample was flushed with high purity argon at 573 K for 1 h to remove water and other contaminants then cooled down to room temperature. A gas mixture containing 5 vol% H_2 in Ar was passed through the sample at a total flow rate of 30 ml min⁻¹. The temperature and detector signals were then continuously recorded while heating at 10 K min⁻¹ up to 1173 K. A cooling trap was also placed between the sample and the detector for removal of released water formed during the reduction process.

 $\rm H_2$ -TPD measurements were conducted in the same equipment as TPR with helium as the carrier gas. About 0.20 g of catalyst was placed in the reactor. The sample was reduced with 5% $\rm H_2/95\%$ Ar (30 ml min⁻¹) at a temperature of 673 K for 2 h. The catalyst was subsequently flushed at the same temperature with helium gas (30 ml min⁻¹) for 30 min. After reduction, the sample was cooled to 303 K, and then $\rm H_2$ flow (30 ml min⁻¹) was continued for 30 min at 303 K. After adsorption, the system was purged with helium gas (30 ml min⁻¹) for 30 min to remove weakly adsorbed species. The $\rm H_2$ -TPD profile was monitored using TCD while the temperature was increased from 303 K to 1173 K at a rate of 10 K min⁻¹. CO₂-TPD and CO-TPD measurements were conducted the same as $\rm H_2$ -TPD, and the adsorption gas was pure CO₂ and CO, respectively.

TG analysis was conducted on a TGA/SDTA851e thermobalance (Mettler Toledo). The thermal analysis data were collected in the range of 308–1173 K in an air flow. The heating rate was 10 K min⁻¹ at a flow rate of 25 ml min⁻¹ while the sample weight was between 7 and 10 mg. TG analysis was used to measure the weight change of the catalysts after reaction.

Results

Catalytic hydrogenation of CO2 into hydrocarbons

Fig. 1(a) presents the CO₂ hydrogenation performances of the FeK/Al₂O₃ catalysts with different SiO₂-coating contents after 8 h (solid line) on stream. Upon initial coating of the catalyst with 1 wt% SiO₂, CO₂ conversion increased, along with a decrease of CO selectivity. The catalysts with more SiO₂-coating at 3 and 5 wt% behaved almost the same and they both give higher CO₂ conversion than with 1Si, which is accompanied by a slight increase of C2+ hydrocarbons selectivity. Upon further increasing the SiO₂ coating up to 7 and 9 wt%, the conversion of CO_2 increased further, together with the additional rise in selectivity of C₂+ hydrocarbons. Moreover, selectivity of byproduct CO decreased significantly in the case of 7Si and 9Si catalyst, while selectivity of methane remained almost the same. However, further increasing SiO₂-coating content from 9 to 11 wt% suppressed the catalyst activity as well as the C2+ hydrocarbons selectivity. Based on these observations 9 wt% was chosen for more study on SiO₂-coating of FeK/Al₂O₃ catalysts for CO₂ hydrogenation.

 C_2 + hydrocarbons selectivities over 0Si and 9Si catalysts are shown in Fig. 1(b). Among all the C_2 + hydrocarbons, propylene,



Fig. 1 (a) Catalyst activity, product selectivity of C₁ and C₂+ with 0–11% SiO₂-coating contents. (b) C₂+ hydrocarbon distribution of OSi and 9Si catalysts. *Reaction conditions*: molar ratio of H₂/CO₂ = 3/1, GHSV = 1800 ml g⁻¹ h⁻¹, P = 3 MPa, T = 673 K.

butylene and ethylene were the major products. It can be seen that SiO_2 -coating could increase long chain hydrocarbons selectivity significantly, and for the 9% coating content catalyst, C_5 + hydrocarbons selectivity increased from 21.9% to 28.0%.

Textural properties

Table 1 gives the BET surface area, pore volume and pore size of the support and catalysts. BET surface area of the 0Si catalyst was about 138 m² g⁻¹; SiO₂-coating first slightly increased the BET surface area of catalysts until the 7Si sample, while the surface area increased slightly from 138 to 144 m² g⁻¹, indicating an effective deposition of silica either on the surface or in the pores of the catalysts. Fig. 2 shows the N2 adsorptiondesorption isotherms of the 0Si, 7Si and 9Si samples (isotherms of the 1-7Si samples are analogous, while 9Si and 11Si samples exhibit virtually the same, see ESI Fig. S1⁺). All samples exhibited typical type IV isotherms with hysteresis loop, according to the IUPAC classification; the isotherm of the catalyst coated with 7% SiO2 was almost the same as the 0Si catalyst. However, a significant decrease in the surface area to 130 m² g⁻¹ was observed, along with a decrease in the pore volume (see Table 1 and Fig. 2) when SiO₂-coating content rose to 9% or more. This apparent decrease in the surface area and pore volume might be due to either the narrowing of the pores or partial blockage of pore entrances by SiO₂ coating at 9 wt% or

Table 1 Physical properties of support and catalysts as prepared

Samples	BET surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Average pore size (nm)	Theoretical content (g M_xO_y per g cat.)			
				SiO_2	Fe ₂ O ₃	K ₂ O	Al_2O_3
γ -Al ₂ O ₃	283	0.42	4.3	_	_	_	1.000
OSi	138	0.21	3.9	_	0.160	0.090	0.750
0Si (cyclohexane) ^a	137	0.21	3.8	_	0.160	0.090	0.750
1Si	140	0.21	3.1	0.01	0.158	0.089	0.743
3Si	142	0.21	3.4	0.03	0.155	0.087	0.728
5Si	143	0.21	3.4	0.05	0.152	0.086	0.713
7Si	144	0.21	3.4	0.07	0.149	0.084	0.698
9Si	130	0.19	3.4	0.09	0.146	0.082	0.683
11Si	130	0.19	3.4	0.11	0.142	0.080	0.668



Fig. 2 $\,$ N_{_{2}} adsorption–desorption isotherm of the OSi, 7Si and 9Si catalysts.

higher, while the depositions of 1-7 wt% SiO₂ were largely dispersed on the surface inside and outside the pores.

Reduction behaviour of catalysts

The reduction behavior of catalysts with different coating content was studied by H_2 -TPR. As shown in Fig. 3, the first



Fig. 3 H_2 TPR profiles of catalysts with different levels of SiO₂ coating on FeK/Al₂O₃.

reduction peak temperature (Fe₂O₃ \rightarrow Fe₃O₄), corresponding H₂ consumption and relative degrees of reduction compared with the 0Si sample are listed in Table 2. Gao et al. concluded from their studies on Fe₂O₃/ γ -Al₂O₃ by TPR and XRD, FeO was metastable at temperature below 840 K, which compared with either Fe₃O₄ or α-Fe.²³ Thus FeO could hardly be detected during the reduction of Fe₂O₃ to Fe. As shown in Fig. 3 and Table 2, coating the alumina supported catalysts with SiO₂ had complex effects on the reduction behavior of iron-based catalysts. Coating a small amount of silica (1-3 wt%) both decreased the reduction temperature and inhibited the reduction degree of iron oxides. After increasing SiO₂-coating content to 5-7 wt%, reduction temperature of iron oxide changed slightly, while reduction degree of iron oxide increased from 71% to 78%. In the case of 9Si sample, the reduction temperature dropped to 754 K, with a minimum reduction degree. Further increasing the coating content to 11 wt% increased both the reduction temperature and reduction degree compared to the 9Si catalyst.

Crystallite structure of catalysts

On the basis of catalyst activity in Fig. 1, 9 wt% is the optimal coating level for CO_2 hydrogenation to hydrocarbons. Among all coated catalysts, BET and TPR results also indicate a

Table 2 Temperature of reduction peak and reduction degree of the catalysts									
Samples	Peak maximum (K)	H ₂ consumption degree ^{<i>a</i>} (%)	Fe content (%)	Reduction degree ^{b} (%)					
0Si	789	100.0	100.0	100					
1Si	773	79.9	99.0	80.8					
3Si	772	69.4	97.0	71.1					
5Si	772	74.8	95.0	78.9					
7Si	776	73.1	93.0	78.5					
9Si	754	63.3	91.0	69.2					
11Si	762	66.7	89.0	75.3					

 a H₂ consumption degree of the catalysts was obtained by comparing total H₂ consumption of 0Si catalyst. b Reduction degree was obtained by regulating H₂ consumption degree with 100% Fe content.

unique character of the 9Si sample. XRD was used to characterize the iron-phase and aluminium-phase structures of the catalysts. XRD patterns of the 0Si and 9Si catalysts as-prepared and after the reaction are presented in Fig. 4. For the fresh catalysts, the XRD patterns of 0Si catalyst exhibited the characteristic diffraction peaks of hematite (α -Fe₂O₃) and alumina (γ -Al₂O₃) while the patterns of SiO₂-coated catalyst changed slightly. After the CO₂ hydrogenation reaction, XRD patterns of both used catalysts exhibited the characteristic peaks of magnetite (Fe₃O₄) and carbide (χ -Fe₅C₂), and χ -Fe₅C₂ is an active phase during the CO and CO₂ hydrogenation. Additionally, the SiO₂-coated catalyst exhibited the characteristic peaks of KFeSi₃O₈ (JCPDS 14-0617) and KAlSiO₄ (JCPDS 11-0579) at $2\theta = 27^{\circ}$ and 28.6° respectively, which were quite different from 0Si sample.

FT-IR

FT-IR spectra of the 0Si and 9Si samples before and after the reaction are shown in Fig. 5. In the spectrum of the fresh 0Si catalyst, two broad bands around 780 and 540 cm⁻¹ were observed, both of which are characteristic bands of Fe–O in the α -Fe₂O₃ phase. With SiO₂-coating, new bands appeared at 1100, 1000 cm⁻¹, which can be attributed to the asymmetric Si–O–Al and Si–O–Fe stretching vibration respectively (base on IR spectra in ESI Fig. S2†). After the CO₂ hydrogenation, 0Si sample exhibited a weak vibration band at 3000 cm⁻¹, assigned to the surface carbon, while the 9Si catalyst showed essentially no peak here. Meanwhile, for the 9Si catalyst, bands at 1100 and 1000 cm⁻¹ became stronger after the CO₂ hydrogenation, which is apparently different from the 0Si catalyst.

Chemical images of the used catalysts (Fig. 6) were recorded on a Nicolet iN10 MX Infrared Imaging Microscope, the colour intensity from *blue* to *red* is proportional to the content of the target molecule, according to the asymmetric vibration at different wavenumbers. Micro-IR spectra were also obtained, as shown in Fig. 6. SiO₂-coated catalyst displayed red at 1000 cm⁻¹ in Fig. 6(d) corresponded to line 3 in Fig. 7(b), confirming the formation of Si–O–Fe structure, while line 4 and 5 showed peaks at 1400 and 1550 cm⁻¹ corresponding to the same structure of line 1 and 2 in Fig. 7(a).



Fig. 4 XRD patterns of fresh and used 0Si and 9Si catalysts. (●): γ -Al₂O₃; (♦): α-Fe₂O₃; (▲): Fe₃O₄; (▼): χ -Fe₅C₂; (▽): KFeSi₃O₈; (△): KAlSiO₄.



Fig. 5 (a) The FT-IR spectra of the fresh OSi and 9Si catalysts. (b) The FT-IR spectra of the OSi and 9Si catalysts after reaction.

H₂, CO₂ and CO chemisorption

TPD measurement was used to investigate the effect of SiO₂coating on the adsorption behaviour of the iron-based catalyst. In Fig. 8(a), H₂ desorption behaviour over SiO₂-coated catalyst was basically the same as the 0Si sample below 800 K. When temperature was higher than 800 K, γ -Al₂O₃ began to transform into θ -Al₂O₃ and α -Al₂O₃, which is accompanied by some weight loss. Weight loss over the SiO₂-coated catalyst was lower compared to the 0Si catalyst, indicating less γ -Al₂O₃ transformations. Similar weight loss over 800 K could also be observed in CO₂ and H₂-TPD profiles as follows.

 CO_2 -TPD profiles of the catalysts are shown in Fig. 8(b). The CO_2 uptakes could be used to indicate the intensity of the surface basicity. In general, there are three desorption peaks in CO_2 -TPD profiles. One peak at the lower temperatures (350–400 K) corresponds to weak CO_2 adsorption, while the other two at higher temperatures (400–550 K, 550–770 K) can be ascribed to the adsorption of CO_2 that interacted moderately with the surface basic site. It was found that peak areas of 400–550 K and 550–770 K decreased after coating the catalyst with SiO₂. Coating the catalyst with SiO₂ resulted in the decrease of iron, potassium and aluminium contents over the entire catalyst (Table 1), while minor potassium result in the decrease of catalyst surface basicity. Therefore the SiO₂-coated sample exhibited weaker CO_2 adsorption capacity.



Fig. 6 (a-c) Micro-IR mappings of the 0Si and 9Si catalysts after reaction. (a) 0Si, 1000 cm⁻¹; (b): 0Si, 1400 cm⁻¹; (c): 0Si, 1550 cm⁻¹. (d-f) Micro-IR mappings of the 0Si and 9Si catalysts after reaction. (d) 9Si, 1000 cm⁻¹; (e) 9Si, 1400 cm⁻¹; (f) 9Si, 1550 cm⁻¹.

Fig. 8(c) presents the CO desorption behavior of the prereduced catalysts. Differing from the 0Si catalyst, a minor peak appeared at 700–800 K in the CO-TPD profile of 9Si sample. Desorption temperature of molecular CO on Fe single-crystal planes were below 473 K, while the dissociative CO desorption occurred at about 770 K. Therefore, adsorption capability of byproduct CO corresponding to desorption temperature of 700– 800 K was enhanced by SiO₂ coating treatment.

TG analysis

The typical TG/DTG curves of the used 0Si and 9Si catalysts are shown in Fig. 9. Both samples displayed a weight loss around 373 K due to the removal of physically adsorbed water. The subsequent weight loss around 573 K was attributed to the removal of crystal water. Weight loss for the 0Si sample was obviously larger than that for the SiO₂-coated below 673 K. The subsequent gradual weight loss above 723 K could be attributed to the decomposition of carbon deposit formed during the CO_2 hydrogenation reaction; the SiO₂-coated catalyst exhibited less carbon deposit. Crystal change of alumina resulted in the weight loss above 800 K, which has been detected in TPD measurement.

Discussion

Iron oxides have tested used as CO₂ hydrogenation catalysts for many years.^{17,24,25} Dorner *et al.* prepared a K and Mn doped iron-



Fig. 7 Micro-IR spectra of the used OSi and 9Si catalysts. (a) OSi catalysts. (b) 9Si catalyst.

based CO2 hydrogenation catalysts, the KAlH4 phase was detected as part of the catalyst's active phase, and K8Mn12Fe17/ Al₂O₃ catalyst performed highest CO₂ conversion (41.4%) and C₂-C₅+ hydrocarbons selectivity (62.4%).¹⁷ Effect of the type of zeolites on catalyst activity for synthesis of iso-alkanes from CO₂ hydrogenation were investigated over Fe-Zn-Zr/zeolites, and HY zeolite was the most effective one for iso-alkane synthesis due to the presence of medium and strong acid sites.²⁴ C₂-C₅+ olefin production from CO2 hydrogenation was investigated using ceria modified FeMnK catalysts, the results showed that the larger ceria particle catalyst (FeMnKCeAl800) performed the best, yielding a CO₂ conversion level of 50.4%.²⁵

Hydrophobicity has been considered a crucial property of coating materials especially due to the recent demand for high temperature performance in various applications, and the SiO_x-DLC (diamond-like carbon) film from the plasma polymerization of HMDSO was chosen to increase the surface hydrophobicity due to its low surface energy compared with a pure DLC film.²⁶ Xu et al. prepared superhydrophobic SiO₂ films from nano-husk ash by sol-gel method using hydroxy silicone oil (HSO), hexamethyldisilazane (HMS), or methyl triethoxysilane (MTS) as modifiers, the results showed that the contact angle of SiO_2 films was more than 160° when volume ratio of the modifiers to silicon-sodium solution (SSS) was 0.15.27 TEOS is widely used as the Si source to alternate the material hydrophobic property. Jeong, Goo and Kim prepared a hydrophobic SiO₂ powder by surface modification of TEOS wet gel with 6 and



(a)

(b)

Intensity (a.u.)

(c)

Intensity (a.u.)



Fig. 8 Desorption of probe gases from OSi and 9Si catalysts. (a) H₂-TPD. (b) CO₂-TPD. (c) CO-TPD.



Fig. 9 TG and DTG curves of the used catalysts: (solid line) OSi; (broken line) 9Si.

12 vol% of TMCS (trimethylchlorosilane).²⁸ Mokhtarimehr *et al.* reported a vanadium doping TiO₂–SiO₂ thin films exhibited significant effect on the hydrophilicity.²⁹ Ghazzal modulated the relative content of TEOS and (methyltriethoxysilane) MTES mixtures in order to modify the hydrophilic–hydrophobic balance of the mesoporous SiO₂ layer.³⁰

Since the synthesis of hydrocarbons by CO₂ hydrogenation over iron-based catalyst can be regarded as a combination of RWGS and F-T synthesis reactions, it is of great importance to enhance the activation of both CO2 and CO. Moreover, byproduct H₂O (from CO₂ hydrogenation) could inhibit CO₂ adsorption on surface, and decrease catalyst activity as well as C₂+ hydrocarbons selectivity. For this reason reducing or eliminating the inhibition of water is of great importance, either in increasing the relative concentration of reactants and reaction intermediate or in overcoming thermodynamic constrains. Improvement of the catalyst hydrophobic property by SiO₂coating process has been proved by the characterization results. The formation of Si-O-Fe and Si-O-Al structures by SiO₂coating treatment can be found in XRD (Fig. 4) and FT-IR (Fig. 5) measurements. Moreover, TPD and TG results indicate a decreasing Al-O-Al amount over the SiO₂-coated catalyst, according to minor weight loss over 800 K by Al₂O₃ crystal phase transformation. SiO2-coating treatment alters the catalyst hydrophobicity by decreasing content of Al-O-H and increasing Si-O-Al content. Removing water generated during the reaction promotes CO₂ and CO hydrogenation to hydrocarbons, and this consideration is supported by catalyst activity data in Fig. 1; coating the catalyst with SiO₂ significantly increases the CO₂ conversion from 49% to 63% when SiO₂ content is 9%, and selectivity toward C₂+ hydrocarbons rises from 64% to 72%. Since CO is the intermediate product in CO₂ hydrogenation, concentration of CO is determined by the relative rates of RWGS, WGS and FTS reaction. However, directly reducing content of CO could not be obtained by promoting RWGS and FTS reactions simultaneously in ways of hydrophobicity improvement.

TPD results indicate that SiO₂-coating alters the adsorption of reactant CO₂ and H₂ and intermediate reactant CO. Too strong a hydrogen adsorption and activation capacity would result in methanation rather than C-C coupling; H2-TPD profiles in Fig. 8(a) illustrates that there is hardly any influences on chemisorption capability of hydrogen, rationalising no change of methane selectivity, as can be seen in Fig. 1(a). Al, Fe and K elemental contents decreased after SiO₂-coating, while K plays the role of basic promoter of the catalyst. CO2-TPD profiles in Fig. 8(b) shows that SiO₂-coating largely reduces the adsorption of CO₂, owing to a lower K content. Since sufficient CO_2 exists in the system, the process of CO_2 activation is more likely the rate-determining step rather than that of CO₂ adsorption. The promotion of RWGS by SiO₂-coating on FeK/ Al₂O₃ catalyst is an important aspect, which can explain at least in part why the SiO₂-coated catalyst with a lower CO₂ adsorption capability exhibits higher activity for CO2 conversion. In the Si-O-Fe structure, there is electron transfer from Fe to Si atoms, showing an electron-deficient state of Fe species.³¹ Due to the triple bond between O and C, carbon atom is the electron-pair acceptor in CO structure; the dissociative adsorption of CO was easier on Fe species with an electron-deficient state. Due to the formation of Si–O–Fe by SiO₂-coating, the coated catalyst facilitates the CO adsorption, which is proved by CO-TPD measurement in Fig. 8(c).

Apart from the CO₂ conversion and product distribution, SiO₂-coating content also affects catalyst physical properties and reduction behavior. BET surface area in Table 1 presents a procedure of the transformation of SiO₂-coating with different SiO₂ content. Initially coating of the Al₂O₃-supported catalyst increases the surface area from 138 to 144 m² g⁻¹; however, when the coating content is 9% or higher, the surface area decreases to 130 m² g⁻¹, accompanied by the reduced pore volume. It is clear that coating content can affect the catalyst physical properties. SiO₂ stays as dispersed tiny particles at SiO₂ content up to 9 wt%, while further increasing coating level enlarges the SiO₂ particles, resulting in the partial blockage of alumina pore entrances. Iron-oxide reduction temperature is also affected by SiO₂-coating, due to the weakened Fe-Al₂O₃ interaction. Adding a small amount of SiO₂ (1-3 wt%) decreases reduction temperature, but also inhibits the reduction of iron oxide. Metal-support interaction is weakened by silica interacting with iron and alumina, leading to a decline of reaction temperature. Such a small amount of SiO₂ is not strong enough to interact directly with iron and alumina to form Si-O-Fe and Si-O-Al species, and the inhibiting effect of reduction degree is due to electron-deficient state of Fe-species in silica-promoted catalysts compared to the silica-free catalyst,³¹ Fe-O bonds are strengthened and become difficult to cleave during the reduction. Upon increasing coating content to 5-7 wt%, reduction temperature changes slightly while reduction degree increases from 71-78%. The excess silica interacts stronger with its neighbouring Al atoms and iron oxides, metal-support interaction become even weaker. Si-O-Fe and Si-O-Al take shape with about 9 wt% coating content, and SiO₂ coating at 9 wt% or higher level might narrowing the pores or become partial blockage of alumina pore entrances according to the BET analysis; the suppression of metal-support interaction decreases the reduction temperature to 754 K; the Si-O-Fe species are hardly reducible, corresponding to decline of reduction degree. With a further increase of coating content to 11%, some iron oxide are covered by surface silica, and interactions between Si and Fe lead to an increase in reduction temperature. Moreover, in order to well disperse on SiO₂, the crystallite size of Fe₂O₃ decreases, causing a higher probability of contact with H₂ during the reduction. Catalyst activity is closely related to the interaction strength between metalsupport and also silica-iron. Weaker metal-support interaction benefits the iron oxide reduction, more active sites are provided for the adsorption and activation of the reactants. Stronger silica-iron interaction profits the adsorption of CO, and the process of F-T synthesis is promoted. When the coating content is 9 wt%, the metal-support interaction is the least, and Si-O-Fe structure is sufficient for CO adsorption compared with other samples, according to the lowest reduction temperature and degree in TPR results. When the coating content is lower than 9%, the promotion of CO adsorption is limited due to weak

It is likely that SiO_2 -coating improved the catalyst hydrophobic property, thereby reducing the negative impact of water by-product and facilitating the reverse water gas shift and subsequent hydrogenation coupled with C–C coupling towards higher CO₂ conversion to long chain hydrocarbons.

Conclusions

RSC Advances

In this study, SiO₂-coating treatment was used to modify the FeK/Al₂O₃ catalyst for CO₂ hydrogenation to hydrocarbons. Coating the catalyst with SiO₂ at desired loading levels largely improved the synthesis of hydrocarbons by CO₂ hydrogenation, likely due to improved catalyst hydrophobic property for reducing the negative impact of water by-product and for restraining WGS. SiO₂-coating also reduced the Fe–Al₂O₃ interaction, resulting in a decrease of iron oxide reduction temperature, along with an enhancement of CO adsorption. Based on the improvements of CO₂ activation and CO adsorption capacity, the optimal coating content is around 9 wt%, where the CO₂ conversion was increased from 49% to 63%, and selectivity of C₂+ hydrocarbons shifted from 63% to 74%.

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