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Effect of lanthanum loading in Fe–K/La–Al_2O_3 catalysts for CO_2 hydrogenation to hydrocarbons†

Sang-Sung Nam,* Gurram Kishan, Myoung-Woo Lee, Myoung-Jae Choi and Kyu-Wan Lee
Chemical Technology Division-I, Korea Research Institute of Chemical Technology, PO Box 107, Yusong, Taejon 305-600, Korea

Lanthanum-modified alumina supports prepared by the impregnation method have been used as supports for potassium-promoted iron catalysts in CO_2 hydrogenation. The catalysts have been characterized by X-ray diffraction, CO_2 chemisorption, temperature-programmed reduction (TPR) and temperature-programmed decarburization (TPDC) techniques. The selectivity towards total hydrocarbons and lower olefins (C_2–C_4) was found to increase with increase in lanthanum content up to 4 wt% in Fe–K/La–Al_2O_3 catalysts and to decrease above this lanthanum content. The TPR profiles of the catalysts of lanthanum-modified Al_2O_3 shows the reduction of Fe_2O_3 to iron(0) follows a three-stage reduction mechanism through formation of the FeO phase. The TPDC profiles show the formation of three types of carbide species on the catalysts during the reaction. The activities of the catalysts are correlated with physico-chemical characteristics of the catalysts. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: CO_2 hydrogenation; hydrocarbon; La–Al_2O_3; iron; potassium; TPR; TPDC

INTRODUCTION

The environmental impact of high concentrations of CO_2 in the atmosphere has been of acute concern to the global community.[1] One of the ways to mitigate this problem is to convert CO_2, at the generation point, to valuable industrial feed stocks, such as lower olefins, and commercially important high molecular weight hydrocarbons. Lower alkenes, such as ethene and propene, are primary feedstocks for the manufacture of polymers and petrochemicals. Production of higher hydrocarbons, in particular the long chain ones, has immense significance, considering that many industrial R&D teams are working towards this goal. Long-chain hydrocarbons, particularly their branched counterparts, can replace aromatics as octane boosters. Iron-based catalysts have shown great promise in the hydrogenation of CO and CO_2. Potassium has been reported to be an effective promoter, as it facilitates elementary steps, reverse water-gas shift (RWGS) and Fischer–Tropsch (F–T) reactions.[2–4] Lee *et al.*[3] have reported higher selectivities for the formation of lower olefins on unsupported Fe–K catalysts in the CO_2 hydrogenation reaction. This selectivity enhancement was attributed to the formation of iron carbides on these catalysts. Several authors[4,5] emphasized the importance of support in iron catalysts for F–T synthesis, as it is expected to influence the iron particle size, reducibility, degree of interaction with the support and the chemical form of species present at the surface of the catalyst. Kishan *et al.*[4] have reported that the Fe–K catalysts supported on Al_2O_3–MgO gives improved selectivity towards the lower olefins and higher hydrocarbons compared with Fe–K catalysts supported either on Al_2O_3 or MgO in CO_2 hydrogenation. There are also several reports[6–10] that the presence of rare earth oxides like lanthanum and cerium exert an influence on various reactions over supported metal catalysts. For instance, Barrault *et al.*[6] reported that lanthanum or cerium oxide promoters improved the total activity and increased the selectivity to alkenes and

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* Correspondence to: Sang-Sung Nam, Chemical Technology Division-I, Korea Research Institute of Chemical Technology, PO Box 107, Yusong, Taejon 305-600, Korea.

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higher hydrocarbons on carbon supported Co and Ru catalysts in CO hydrogenation. The stability of the support is the most important factor governing the life. It has been found that the addition of a lanthanide oxide to Al_2O_3 retards the transformation (through sintering) of γ-Al_2O_3 to α-Al_2O_3.[11,12] The presence of the perovskite-type structure of lanthanide aluminate could be responsible for the thermal stabilization of such transition alumina.[11,12] Thus the presence of lanthanum is known to stabilize the alumina support and enhance the selectivity of higher hydrocarbons in CO hydrogenation.

In the present study, we have used lanthanum-modified Al_2O_3 as supports for potassium-promoted iron catalysts in CO_2 hydrogenation. These catalysts have been characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed decarburization (TPDC) and CO_2 chemisorption. An attempt has also been made to correlate the results with hydrocarbon distribution in CO_2 hydrogenation.

EXPERIMENTAL PROCEDURE

Different La–Al_2O_3 ratio supports were prepared by impregnating Al_2O_3 with the required amounts of lanthanum nitrate. The supports were dried and calcined at 773 K for 8 h. 20 wt% Fe–K catalysts supported on the above lanthanum-modified aluminas were prepared by impregnating supports with the required amounts of iron nitrate and potassium carbonate. The atomic ratio of Fe:K is maintained as 2:1. The catalysts were dried and calcined at 773 K for 24 h.

Powder XRD patterns of supports and catalysts were recorded using a Rigaku 2155D6 X-ray diffractometer with nickel-filtered Cu Kα radiation. Chemisorption of CO_2 was performed using a conventional high-vacuum volumetric chemisorption apparatus (Micromeritics, ASAP 2400) by the double-isotherm method at 298 K.[4] Prior to the adsorption measurements, the samples were reduced in a flow of hydrogen at 723 K for 16 h and the catalyst cell was evacuated and cooled to room temperature under dynamic vacuum ($<10^{-5}$ Torr).

For TPR studies, 50 mg of the calcined catalyst was loaded in a quartz reactor and heated at 673 K for 6 h under argon atmosphere. After cooling the sample to room temperature, a high-purity premixed gas containing 95% argon and 5% hydrogen was used as a reducing agent. TPR profiles were collected while the catalyst was heated linearly at 5 K min^{-1}. Traces of oxygen and water were removed by passing through an activated molecular sieve trap kept in an ice bath.

Prior to decarburization experiments, 200 mg of catalyst was reduced at 623 K in hydrogen for 24 h. The reduced catalyst was exposed to H_2/CO_2 (3/1) mixed gas at 573 K and 1 atm for 4 h. After the reaction the catalyst bed was quickly cooled down to room temperature in argon gas. Then argon was replaced by hydrogen gas and TPDC profiles were obtained while raising the temperature of the catalyst lineraly to 973 K at 5 K min^{-1}. It was found that the product was almost exclusively methane (over 99%).

Hydrogenation of CO_2 was carried out in a fixed-bed flow reactor made of stainless steel (10 mm i.d. and 200 mm length). The particle size of the catalysts was maintained between 25 and 40 mesh. Prior to introducing the reactant gas mixture ($H_2/CO_2 = 3$) into the reactor, the catalyst was reduced in hydrogen at 723 K for 24 h. The reaction was carried out at 573 K and at 10 atm pressure for 24 h. The gas transfer line from the reactor to the gas chromatograph (Chrompak CP 9001) was equipped with thermal conductivity (Porapak Q column) and flame ionization (GS-Q capillary column) detectors.

RESULTS AND DISCUSSION

The XRD data show that there are no peaks corresponding to iron and potassium in all the samples, which indicates that iron and potassium are well dispersed on the surface of the supports. The results of CO_2 hydrogenation to hydrocarbons are summarized in Table 1. It is clear from Table 1 that CO_2 conversion, selectivity to CO and total hydrocarbons vary based on the support composition (Fig. 1). The conversion of CO_2 increased with increase in lanthanum content in the support composition. The total hydrocarbons and selectivity towards C_2–C_4 olefins in the products increased with increasing lanthanum content, peaking at 4 wt%, whereas further increases in the lanthanum content of the support had the opposite effect. These results may be attributed to an increase in the basicity of the catalysts, as revealed by the increase in CO_2 chemisorption with lanthanum content of the support. Our previous results[4] also clearly indicate that the CO_2 conversion, selectivities of total hydrocarbons, C_2–C_4 olefins and higher

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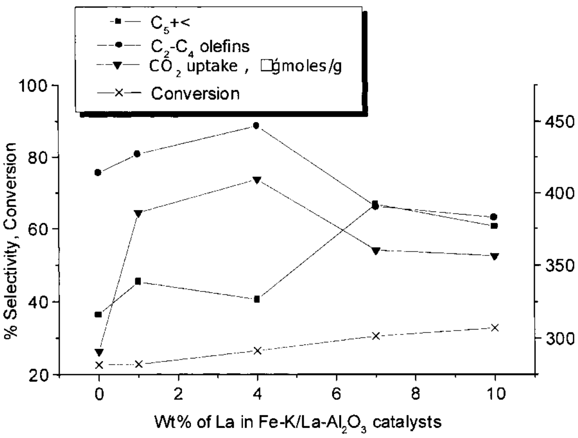

Figure 1 Dependence of total hydrocarbon, C_2–C_4 olefin selectivities, and CO_2 chemisorption over support composition in Fe–K/La–Al_2O_3 catalysts.

Table 1 BET surface area and CO_2 chemisorption values of Fe–K catalysts supported on La–Al_2O_3

Catalyst	BET surface area (m^2 g^{-1})	CO_2 uptake (mol g^{-1})
Fe–K/Al_2O_3	95	290.8
Fe–K/La(1)–Al_2O_3 (99)	110	385.9
Fe–K/La(4)–Al_2O_3 (96)	106	409.2
Fe–K/La(7)–Al_2O_3 (93)	101	359.9
Fe–K/La(10)–Al_2O_3 (90)	85	356.2

hydrocarbons depend on the support composition in Fe–K/Al_2O_3–MgO catalysts; an optiomal concentration of about 20 wt% of MgO offers the highest selectivity to olefins. The selectivity of higher hydrocarbons increases with increasing lanthanum content, whereas the selectivity of methane decreased with increasing lanthanum content in Fe–K/La–Al_2O_3 catalysts. Dry and Oosthuizen[13] had also observed a decrease in methane selectivity with enhanced CO_2 chemisorption on alkali-metal-promoted iron catalysts supported on SiO_2. In all the catalysts the major part of the CO_2 is converted into high molecular weight hydrocarbons. The increase of higher hydrocarbons with lanthanum content might be due to chain growth probability of lanthanum. Several authors[14] also reported that the presence of lanthanum increases the chain growth probability (alpha) in F–T synthesis. A major part of the olefinic content is constituted by C_3 olefins. It is also interesting to note that in each carbon number the olefinic content is much higher than the paraffinic content, which is very important in polymers and the petrochemical industry.

Barrault *et al.*[6] reported that the addition of lanthanum to cobalt supported on carbon catalysts increased the selectivity for C_2–C_4 fraction and this fraction is essentially olefinic in CO hydrogenation. These authors believed that the enhanced activity is an indication of the formation of new sites. Pettigrew et al.[9] also reported an enhancement in

Table 2 CO_2 hydrogenation[a] over Fe–K catalysts supported on La–Al_2O_3

Catalyst (Fe: 20wt%) (Fe:K = 2:1)	Fe–K/Al_2O_3	Fe–K/La–Al_2O_3 (1:99)	Fe–K/La–Al_2O_3 (4:96)	Fe–K/La–Al_2O_3 (7:93)	Fe–K/La–Al_2O_3 (10:99)
CO_2 conv. (%)	22.6	22.8	26.5	30.51	32.75
Selectivity (C mol%)					
CO	40.6	40.9	18.7	26.9	28.8
—HC—	59.4	59.1	81.3	73.1	71.2
Hydrocarbon distribution (C mol%)					
C1	16.3	14.3	13.9	5.85	4.36
C2=	10.5	9.45	10.4	3.50	3.49
C2	3.40	2.41	2.3	1.16	1.25
C3=	14.3	15.2	15.3	5.77	5.21
C3	3.30	0	2.210	5.86	4.87
C4=	12.2	11.2	14.5	8.84	6.32
C4	3.40	2.1	0.58	2.29	1.95
C5>	36.4	45.3	40.5	66.7	60.6
Selectivity of olefin (C_2–C_4) *(C mol%)*					
Ol./(Ol. + Para.)	75.5	80.8	88.6	66.1	63.0

[a] CO_2 hydrogenation at 1900 ml/g^{-1} h^{-1} 573 K, and 10 atm.

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activity in the RWGS reaction by modifying the alumina support with lanthanum in palladium catalysts.

The CO_2 uptake values increased with increasing lanthanum content up to 4 wt% in the catalysts, while a further increase in lanthanum content led to a decrease. A good correlation was found between the CO_2 hydrogenation activity results and chemisorption uptakes (Fig. 1). It is evident from Fig. 1 that the selectivities of total hydrocarbons and lower (C_2–C_4) olefins correlate with CO_2 uptakes.

The TPR profiles of Fe–K catalysts supported on La–Al_2O_3 catalysts are shown in Fig. 2. They indicate a two- or three-stage reduction mechanism depending on the support composition. There is general agreement that the reduction of the bulk phase α-Fe_2O_3 proceeds in the following steps:

$$\underset{\text{haematite}}{\alpha\text{-}Fe_2O_3} \longrightarrow \underset{\text{magnetite}}{Fe_3O_4} \longrightarrow \underset{\text{wustite}}{FeO} \longrightarrow \underset{\text{iron}}{\alpha\text{-}Fe}$$

The TPR profile of the Fe–K/Al_2O_3 catalyst shows a two-stage reduction, the first step being at around 733 K and the second one at 945 K. It is the second peak that has shifted to higher temperatures with increasing lanthanum content in the catalyst. Usually the first peak is attributed to reduction of Fe_2O_3 (haematite) to Fe_3O_4 (magnetite), whereas the second peak is attributed to the reduction of Fe_3O_4 to iron metal. We did not observe any peak corresponding to the formation of metastable FeO or iron(II) aluminate for the Fe–K/Al_2O_3 catalyst. However, for Fe–K/La–Al_2O_3 catalysts a three-stage reduction profile has been observed. The middle peak may be attributed to transformation of Fe_3O_4 to FeO. Bulk-phase FeO is thermodynamically metastable compared with either magnetite or α-Fe at temperatures below 840 K.[15] However, in the presence of certain oxide supports, FeO may be stabilized and the stability of FeO on different oxide supports can be used to estimate the extent of the iron-oxide–support interaction.[4,16] In these catalysts, there exists a strong interaction between surface iron oxide with the mixed lanthanum-modified alumina support. In particular, the Fe–K/La(4)–Al_2O_3(96) catalyst has a high peak area at 820 K, which is believed to be responsible for the formation of active iron carbides. Several authors[2,4,16] also reported that the iron carbides, which are reported to be active in CO_2 hydrogenation, have been speculated to be formed either from FeO or α-Fe. Our reaction results are confirmed by the TPR profiles.

TPDC profiles of Fe–K catalysts supported on La–Al_2O_3 are shown in Fig. 3. All TPDC profiles show a single predominant peak with a peak maximum temperature shifting from 800 to 923 K when the lanthanum content is increased from 0 to 10% in the catalyst support. This shows that the stability of the surface carbides has increased with increasing lanthanum content. The amount of carbide increased with lanthanum contents up to 4

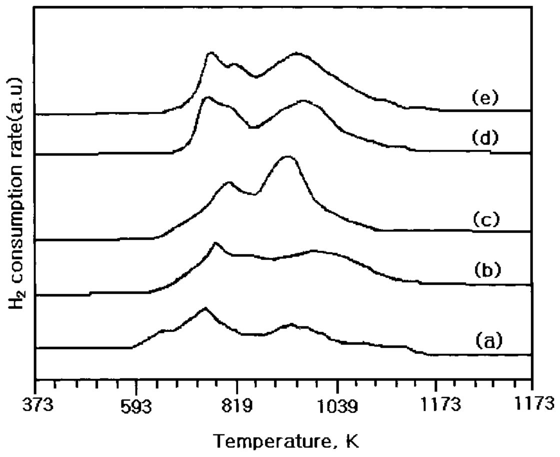

Figure 2 The TPR profiles of 20 wt% Fe–K catalysts with different La–Al_2O_3 proportions: (a) Fe–K/Al_2O_3; (b) Fe–K/La(1)–Al_2O_3(99); (c) Fe–K/La(4)–Al_2O_3(96); (d) Fe–K/La(7)–Al_2O_3(93); (e) Fe–K/La(10)–Al_2O_3(90).

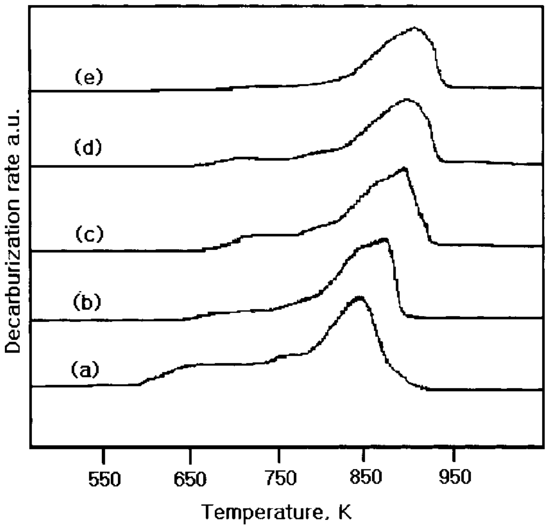

Figure 3 The TPDC profiles of 20 wt% Fe–K catalysts with different La–Al_2O_3 proportions: (a) Fe–K/Al_2O_3; (b) Fe–K/La(1)–Al_2O_3(99); (c) Fe–K/La(4)–Al_2O_3(96); (d) Fe–K/La(7)–Al_2O_3(93); (e) Fe–K/La(10)–Al_2O_3(90).

wt% in Fe–K/La–Al_2O_3 catalysts, but further increases in lanthanum content led to a decrease. For all the catalysts, two small broad humps were observed prior to the main peak and the areas of these peaks were highest for the Fe–K/La(4)–Al_2O_3(96) catalyst. These peaks may represent either the presence of other carbides with different stabilities or another decarburization pathway due to metal–support interactions. Barbier *et al.*[17] reported a relation between the selectivity and the extent of carbide formation in F–T synthesis over supported nickel catalysts. For our studies also, the area of the main peak increased with increase in lanthanum content up to 4 wt% in the catalyst and a decrease beyond this lanthanum loading. The formation of larger quantities of these carbides would increase the chain growth probability and increase the selectivity of olefins and C_{5+} hydrocarbons as discussed for the activity results. The similarity between the TPR peaks, particularly the peak at 820 K, and the main TPDC peaks shows that a close relationship exists between the reduction of Fe_3O_4 to FeO, the formation of carbide structures and the activity in CO_2 hydrogenation over these catalysts.

CONCLUSIONS

The results of an XRD study of the catalysts reveal that iron and potassium are well dispersed over La–Al_2O_3 supports. The conversion of CO_2 and the selectivity of higher hydrocarbons increased with increase in lanthanum content. The TPR profiles of the catalysts of lanthanum-modified Al_2O_3 show that the reduction of Fe_2O_3 to iron(0) follows a three-stage reduction mechanism through formation of FeO phase. The TPDC profiles show the formation of three types of carbide species on the catalysts during the reaction. The selectivity of lower olefins (C_2–C_4) and total hydrocarbon selectivity are found to increase in the same way as CO_2 chemisorption and the areas of the TPDC and TPR peaks corresponding to reduction of Fe_3O_4 to FeO of the catalysts.

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