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Selective Synthesis of C_2-C_4 Olefins and C_{5+} Hydrocarbons over Unpromoted and Cerium-promoted Iron Catalysts Supported on Ion Exchanged (H, K) Zeolite-Y[†]

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Hydrogenation of CO_2 to hydrocarbons is carried out on unpromoted and Ce-promoted iron catalysts supported on ion exchanged (H, K) zeolite-Y; the results suggest that the Fe–Ce/KY catalyst has significant advantages being highly selective for C_2-C_4 olefins and C_{5+} hydrocarbons.

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, into 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.[2–4] Potassium has been reported to be an effective promoter, as it facilitates elementary steps, reverse water-gas shift (RWGS) and Fischer–Tropsch (FT) reactions.[2–4] Lee *et al.*[2,3] 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. There were several reports[5–8] that the presence of rare earth metal oxides like La and Ce exert an influence on CO hydrogenation over supported metal catalysts. For instance, Barrault *et al.*[5] reported that lanthanum or cerium oxide promoters improved the total activity and increased the selectivity to alkenes and higher hydrocarbons on carbon-supported cobalt and ruthenium catalysts. However, there were no reports pertaining to CO_2 hydrogenation (unlike CO hydrogenation), in which selective synthesis of both the lower olefins and long chain hydrocarbons has been achieved. The present study reports selective synthesis of C_2-C_4 olefins and C_{5+} hydrocarbons on Ce-promoted iron catalysts supported on potassium exchanged zeolite-Y. The results have been compared with the results obtained on unpromoted catalysts.

The ion exchanged (H, K) zeolite-Y was prepared as described elsewhere[9] and the crystallinity of the thus obtained material was verified by XRD. To prepare unpromoted and Ce-promoted catalysts, the H, K-Y zeolites were impregnated with corresponding aqueous solutions of iron nitrate and iron nitrate + cerium nitrate (17 wt% Fe, atomic ratio of Fe:Ce was 9:1) through the incipient wetness method. Thus obtained catalysts were dried at 383 K for 16 h and calcined in air at 773 K for 24 h. Chemisorption measurements of CO_2 were carried out at 298 K by the double isotherm method, after reducing the catalyst at 723 K for 16 h in hydrogen. Hydrogenation of CO_2 was carried out in a fixed bed flow reactor made of stainless steel. Prior to the initiation of the reaction the catalyst was reduced *in situ* in hydrogen at 723 K for 24 h. The reaction was carried out at 573 K under 10 atm, using a reactant gas mixture in the ratio $H_2/ : CO_2 = 3 : 1$ at a flow rate of $1900\ ml\ g^{-1}\ h^{-1}$. Products were analysed by on-line GC using both FID and TCD with the help of GS-Q capillary and Porapack Q columns respectively.

Reaction results are compared in Table 1. Methane was found to be the major product on Fe/HY catalyst. The CO_2 conversion was also not that high, the major part being converted into CO and saturated hydrocarbons. The presence of potassium not only increased the conversion of CO_2, tremendous improvements also being observed in selectivities to desired products such as olefins and higher hydrocarbons. This clearly shows that the potassium exchanged catalyst has a bifunctional character as it not only increases the conversion but also alters the hydrocarbon distribution. On the other hand, the highly acidic Fe/HY catalyst produced mainly methane. The high selectivity for methane can be attributed to the low concentration of active carbon on the surface, which is due to low dissociation of CO_2 for acidic catalysts.[10] The presence of potassium in Fe/KY is expected to enrich the local electron density of the active iron metal.[11] There are several reports in the literature of improved selectivities upon potassium addition to iron catalysts.[2,3] It is speculated that potassium strengthens the

Table 1 CO_2 hydrogenation[a] over unpromoted and Ce-promoted iron catalysts supported on HY and KY zeolites

Catalyst (17 wt%)	Fe/HY	Fe/KY	Fe-Ce/HY	Fe-Ce/KY
CO_2 conversion	10.14	17.95	11.58	20.08
Selectivity (C mol%)				
CO	39.14	31.35	31.33	34.61
HC	60.86	66.49	68.67	65.39
Hydrocarbon distribution (C mol%)				
C_1	72.56	12.54	70.48	8.86
$C_2^=$	0.02	8.94	0.02	8.73
C_2	15.23	3.18	10.23	2.21
$C_3^=$	0.07	13.02	4.96	15.79
C_3	7.64	3.24	—	—
$C_4^=$	—	10.40	2.73	12.19
C_4	2.98	3.83	0.74	2.62
C_{5+}	1.49	44.50	10.83	49.59
Selectivity for olefins (C_2-C_4) (C mol%)				
Ol./(Ol. + Para.)	0.36	75.93	41.29	88.37

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

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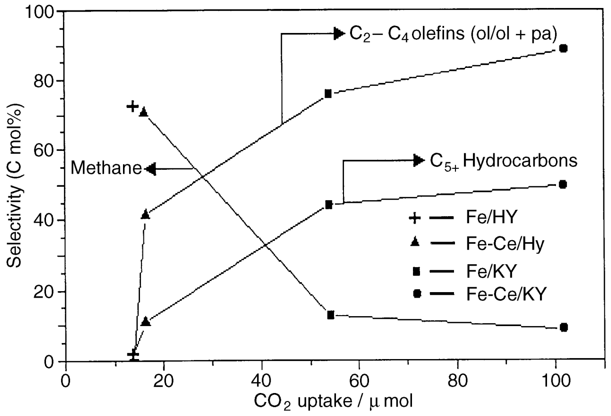

Fig. 1 Correlation between CO_2 chemisorption and hydrocarbon distribution over unpromoted and Ce-promoted catalysts supported on (H, K) zeolite-Y

bond between iron and carbon, while simultaneously weakening the carbon–oxygen bond, facilitating easier formation of a C-H bond. Some reports suggest that the olefin formation is initiated through an iron carbide mechanism.[2,3] Our temperature programmed decarburization results concur with those observations, as increased quantities of carbide species has been observed on Fe/KY catalysts. Higher uptake of CO_2 (Fig. 1) is a further proof of the enhanced basicity of the potassium promoted catalyst.

The CO_2 conversion, selectivity to CO and total hydrocarbons on Fe-Ce/HY catalyst was not significantly different to that with Fe/HY catalyst. Moreover, the CO_2 conversion increased marginally and the selectivity of olefins increased markedly from 0.36 to 41.29. This enhancement might be due to formation of new active sites. Barrault *et al.*[5] also observed the enhancement of selectivity for C_2-C_4 olefins with cerium promoted CO catalysts supported on carbon. Cerium promoted iron supported on a KY catalyst showed improved selectivity for C_2-C_4 olefins and high molecular weight hydrocarbons compared with that of Fe/KY catalysts. Some sort of synergy appears to be responsible for this enhanced selectivity of both C_2-C_4 olefins and C_{5+} hydrocarbons, as cerium promotion alone (in Fe–Ce/HY) did not result in this enhancement. The promotion effect of cerium oxide might be due to partially reduced cerium oxide, which provides binding sites for the oxygen ends of the carbon dioxide molecule facilitating its dissociation. These results agree with those on ruthenium/alumina catalysts promoted by cerium oxide.[12,13] The promotion effect has been explained in terms of newly formed active sites (metal–promoter ensembles) at which the carbon monoxide is bonded with its carbon atom to a metal atom and with its oxygen atom to a partially reduced promoter ion.[14] This arrangement results in the weakening of the C–O bond, and so in enhanced dissociation of CO_2. As discussed above, the potassium will also enhance the dissociation of CO_2. The combined effect of potassium ion exchanged Y zeolite and cerium oxide has enhanced the selectivities of C_2-C_4 olefins and C_{5+} hydrocarbons. Another feature of these catalysts is reduction of methane, which is also a greenhouse gas. As can be seen from Fig. 1, there is some trend of CO_2 uptake and selectivity of methane, C_{5+} hydrocarbons and C_2-C_4 olefins. Formation of large amounts of C_{5+} hydrocarbons on cerium-promoted basic Y zeolites may be explained through polymerization of $(CH_x)_{ad}$ species followed by hydrogenation of the surface hydrocarbon precursors.[15] Here, both an increase of the rate of C-O bond dissociation and/ or a decrease of the hydrogenation rate of surface carbon species can contribute to the enhanced formation of long chain hydrocarbons. Moreover, a decreased hydrogenation rate, which could be related with a lower population and mobility of hydrogen atoms over the oxide promoted catalysts, may facilitate the formation of olefinic hydrocarbons. Lower hydrogen uptake over these catalysts further supports this argument. Thus our results clearly show that though cerium alone is not a good promoter, its coexistence with potassium indeed improves the performance in selective synthesis of C_{5+} hydrocarbons and C_2-C_4 olefins in CO_2 hydrogenation.

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