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Catalysis Today 24 (1995) 371–375

CATALYSIS TODAY

The regularities in the interaction of alkanes with CO_2 on oxide catalysts

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Abstract

Catalytic oxidation of C_1–C_7 alkanes by CO_2 as a non-traditional oxidant was studied on oxide catalysts. The supported manganese oxide catalysts are the most active, selective and stable. Methane is converted mainly into synthesis gas. Ethane and propane give products of oxidative dehydrogenation. In the case of C_4–C_7 alkanes at first direct dehydrogenation takes place and after that reverse water gas shift proceeds.

Reactions of carbon dioxide with hydrocarbons were up to now still insufficiently studied. This is caused by small reactivity of both CO_2 and hydrocarbons. The recent interest in carbon dioxide reactions is two-fold: 1) the necessity to fight against the so-called green-house effect and 2) the exhaustion of raw carbon material sources [1].

The CO_2 molecule can be used a non-traditional oxidant. The best reducing agent for CO_2 is hydrogen. It was shown [2] that methanol synthesis proceeds not by direct $CO + H_2$ interaction, but by preliminary CO transformation into CO_2

$$CO + H_2O = CO_2 + H_2 \qquad (1)$$

After that the interaction of CO_2 with H_2 gives methanol

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (2)$$

But hydrogen is expensive. Hydrocarbons in the role of CO_2 reductants are more attractive.

The most intensively studied reaction of hydrocarbons with CO_2 is methane conversion into synthesis gas

$$CH_4 + CO_2 = 2H_2 + 2CO \qquad (3)$$

The main difficulty encountered when this reaction is used for the practical process of synthesis gas production is coking of the metal catalysts [3–6].

We have studied C_1–C_7 interaction with CO_2 over oxide catalysts [7–10] and it turned out that manganese oxides containing catalysts are effective both for methane transformation into synthesis gas and for C_2–C_7 alkanes dehydrogenation and oxidative cracking. What is especially important is that these catalysts are very stable during a long period without cake accumulation. This paper provides a review of our work in this field.

1. Methane conversion

The interaction of methane with CO_2 was studied on different oxide catalysts [7–9]. Under stationary conditions the 5%Ca– 12%Mn–O/Al_2O_3 catalysts were the best ones. In the stationary state the reaction (3) of synthesis gas formation proceeds. At 930°C complete CO_2 and CH_4 consumption reaches 99.7% with CO selectivity and 84.6% with H_2 selectivity. The activity is stable

SSDI 0920-5861(95)00061-5

during a very long period and coke is not formed.

An XRD study shows that oxidized Mn phases: Mn_2O_3 and Mn_3O_4 promote total methane oxidation while the reduced phases: MnO and $MnCO_3$ assist methane conversion into synthesis gas. A comparison of H_2 formation in steady state conditions ($3 \cdot 10^{-3}$ mol/g·hour at 870°C) and during the reduction of the catalyst by methane ($1.7 \cdot 10^{3}$ mol/g·hour) show that they are close to each other. Methane activation but not the CO_2 activation is the probable rate controlling step. The stationary MnO phase is stable during catalysts and prevents coking. The most probable scheme of CH_4 conversion with CO_2 is the following one:

$$CH_4 + MnO \xrightarrow{K_1} MnO\ldots C + 2H_2$$

$$CO_2 + MnO \xrightarrow{K_2} MnCO_3 \qquad (4)$$

$$MnCO_3 + MnO\ldots C \xrightarrow{K_3} 2MnO + 2CO$$

$$MnCO_3 + H_2 \rightarrow MnO + CO + H_2O$$

$$Mn\ldots C + H_2O \rightarrow MnO + CO + H_2$$

Kinetic equation for the rate of H_2 formation follows from the scheme (4)

$$r = \frac{k_1 P_{CH_4}}{1 + \frac{1}{k_2 k_3} \frac{P_{CO}^2}{P_{CO_2}} + k_2 P_{CO_2}} \qquad (5)$$

where P_{CH4}, P_{CO}, P_{CO2} are partial pressures of CH_4, CO, CO_2, correspondingly. This equation is different from the kinetic equations of reaction (3) for metallic catalysts [3].

The 1.5%K–5.5%Cr–17%Mn–O/SiO_2 catalyst shows different properties. CO prevails in the reaction products in conformity with reaction (6)

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \qquad (6)$$

Methane oxidative coupling, reaction (7) and (8) were also observed on some catalysts

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O \qquad (7)$$

$$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O \qquad (8)$$

At 800°C ΔG for the reaction (7) is positive but not very high. The equilibrium yield of C_2H_6 at 800°C is equal to 13% which is a high enough value.

On the well known Li/MgO catalyst for methane oxidative coupling both the methane oxidative coupling by CO_2 with C_2 hydrocarbons formation, reactions (7) and (8) and the synthesis gas formation (3) were observed. In the stationary state methane conversion at 800°C, V = 1800 hour^{-1} and $CH_4/CO_2 = 5$ was 10.8% and the rate of synthesis gas formation was 2.5 times higher than that of ethylene formation.

2. Ethane conversion

During ethane interaction with CO_2 both ethane oxidative dehydrogenation (8) and synthesis gas formation (9) proceed

$$C_2H_6 + 2CO_2 \rightarrow 4CO + 3H_2 \qquad (9)$$

The most active and stable catalysts for the reactions (8) and (9) were also manganese oxides based catalysts [7,10]. On the 17%MnO/SiO_2 catalyst C_2H_6 conversion of 73.1% and CO_2 conversion of 49.0% were observed at 800°C, V = 3600 hour^{-1} and CO:C_2H_6 = 1.5. C_2H_4 selectivity was 61.0% and C_2H_4 yield = 44.5%. A similar catalyst supported on Al_2O_3 displayed a much lesser selectivity. On the nickel catalyst the $C_2H_6 + CO_2$ reaction proceeds non-selectively with formation of CO, H_2 and coke.

We have studied also the effect of modifying additions to Mn oxides of a series of oxides which are known as dehydrogenation catalysts (Sb, Zn, V, Fe, Cr oxides). The most active and selective catalyst for C_2H_4 production was found to be 5.5%Cr–17%Mn–O/SiO_2. Further increase of selectivity was observed upon additional modification by alkali metal oxides. The 1.5%K–5.5%Cr–17%Mn–O/SiO_2 catalyst shows at 830°C C_2H_6 conversion 82.6%, CO_2 conversion 55.7% and C_2H_4 selectivity 76.8%.

The rate of ethane dehydrogenation by carbon dioxide is described by the equation (10)

$$r_{C_2H_4} = \frac{K_1 P_{C_2H_6} K_{ox} P_{CO_2}}{K_{ox} P_{CO_2} + K_{red} P_{CO}} \qquad (10)$$

where K_{ox} and K_{red} are rate constants of the catalyst oxidation and reduction. The equation (10) describes the observed decrease of selectivity with conversion. This redox equation differs from the corresponding redox equation for alkane oxidation by oxygen where the denominator consists of the sum $K_{ox}P_{O2} + K_{red}P_{CnHm}$.

The mechanism of ethane dehydrogenation by CO_2 on the K–Cr–Mn–O/SiO_2 catalyst can be presented by the scheme (11)

$$\begin{aligned}
&C_2H_6 + Cr^{3+}O^{2-} \rightarrow C_2H_5 + Cr^{2+}OH^-\\
&C_2H_5 + Cr^{3+}O^{2-} \rightarrow C_2H_4 + Cr^{2+}OH^-\\
&C_2H_6 + MnCO_3 \rightarrow C_2H_4 + MnO + CO + H_2O\\
&2Cr^{2+}OH^- \rightarrow Cr^{2+}O^{2-}Cr^{2+} + H_2O \qquad (11)\\
&Cr^{2+}O^{2-}Cr^{2+} + MnCO_3 \rightarrow 2Cr^{3+}O^{2-}\\
&\quad + MnO + CO\\
&MnO + CO_2 \rightleftharpoons MnCO_3C_2H_6 \rightarrow C_2H_4 + H_2
\end{aligned}$$

The scheme (11) explains the higher yields of CO as compared to CH_4 where the following CO/H_2 ratios were obtained: $CO/H_2 = 5–8$ at 700°C and 1.5–2 at 830°C. This means that the role of the last reaction in the scheme (11), thermal dehydrogenation, is relatively small.

The redox mechanism of manganese carbonate decomposition on the phase boundary MnO–CrO seems to play here an important role.

$$\begin{aligned}
&MnO\ldots Cr^{2+}O^{2-}Cr^{2+}O^{2-} + CO_2\\
&\quad \rightarrow MnCO_3\ldots Cr^{2+}O^{2-}Cr^{2+}O^{2-} \qquad (12)\\
&\quad \rightarrow MnO + CO + O^{2-}Cr^{3+}O^{2-}Cr^{3+}O^{2-}
\end{aligned}$$

The chromium oxide phase is reduced and oxidized and the manganese oxide takes part in the reoxidation by CO_2.

The sites basicity determines the stability of carbonate structure and, as a consequence, the degree of redox sites reoxidation. Basic sites of moderate basicity are necessary for CO_2 absorption and Cr^{3+} reoxidation.

3. Propane conversion

Propane interaction with CO_2 can proceed on different catalysts by three reactions

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O \qquad (13)$$

$$2C_3H_8 + 2CO_2 \rightarrow 3C_2H_4 + 2CO + 2H_2O \qquad (14)$$

$$C_3H_8 + 3CO_2 \rightarrow 6CO + 4H_2 \qquad (15)$$

Manganese oxides were in this case also the most active and stable ones [8]. On nickel catalyst the CO_2 conversion in an equimolar $C_3H_8 + CO_2$ mixture was at 750°C as high as 80–85%, but propane transforms into CO and H_2 and the process is characterized by quick coking.

The best catalyst for selective propane conversion with CO_2 is also 1.5% K–5.5%Cr–17%Mn–O/SiO_2. The yield of C_2–C_3 olefins at 830°C, 3600 $hour^{-1}$ and CO_2/C_3H_8 is 73% (80% of its C_2H_4), propane conversion is 96% and the ratio CO/$(C_2H_4 + C_3H_6) = 1.4$. At 800°C the ratio CO/$(C_2H_4 + C_3H_6)$ increases up to 4. With increase of conversion a considerable olefins selectivity decrease is observed. Such a trend can be explained by a higher degree of hydrocarbon conversion and by production of a more reduced mixture than in the case of ethane. The amount of coke after a long period of steady state reaction does not exceed 3.6% in respect to the mass of the catalyst.

The general trends of propane conversion with CO_2 are similar to those for ethane transformation.

The rate of selective transformation of C_3H_8 with CO_2 into ethylene is described by the equation

$$r_{C_2H_4} = \frac{K_1 K_{red} P_{C_3H_8} K_{ox} P_{CO_2}}{K_{red} P_{CO_2} + K_{ox} P_{CO}} \qquad (16)$$

which is very similar to the equation (10). The rate of the catalyst reduction by C_3H_8 is 17 times less than the rate of the reduction by CO.

4. Isobutane conversion

The degree of C_4H_{10} dehydrogenation into C_4H_8 is 19% at 665°C, but CO_2 is not involved in the reaction. The Cr–MnO/SiO_2 catalyst is active for oxidative dehydrogenation by CO_2.

$$i\text{-}C_4H_{10} + CO_2 = i\text{-}C_4H_8 + CO + H_2O \qquad (17)$$

It shows C_4H_{10} conversion of 61–66%, CO_2 conversion of 20–29.5% and $i\text{-}C_4H_8$ selectivity of 78–81%. CO and H_2 are formed in equal amounts this being explained by the equilibrium reaction (1).

The kinetic equation of the process has the form (18) similar to the Mars–Van Krevelen:

$$r_{i\text{-}C_4H_8} = \frac{K_1 P_{i\text{-}C_4H_{10}} K_2 P_{CO_2}}{K_1 P_{CO_2} + K_2 P_{i\text{-}C_4H_{10}}} \qquad (18)$$

It differs from the equations (10) and (16) for ethane and propane. Thus the catalyst reduction by CO formed during the reaction is less significant than the catalyst reduction by isobutane.

A study of the $H_2 + CO_2$ reaction on the same catalyst showed that the rate of CO formation is close to the rate of CO formation in steady state conditions of the reaction (17). The rate of CO formation during CO_2 interaction with the reduced Cr- or Mn–O/SiO_2 catalyst

$$CO_2 + \square \rightarrow CO + O_{adc} \qquad (19)$$

is also considerably (10 times) less than the rate of CO formation in the steady state conditions.

Thus the main route of the CO formation is reaction (1) and the reaction (17) proceeds mainly by two consecutive reactions

$$i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_8 + H_2 \qquad (20)$$

$$CO_2 + H_2 \rightleftharpoons H_2O + CO \qquad (1)$$

The hydrogen formed upon isobutane dehydrogenation is not oxidized completely; only about a half of the H_2 participates in the subsequent CO_2 reduction in accordance with the equilibrium of the reaction (1) at 660°C. CO_2 in the reaction (1) is transformed into CO not by the reaction (19) but probably through intermediate formation of $HCOO^-$ complex and its decomposition into $CO + OH^-$. A special investigation showed that small additions of hydrogen (1–3%) to CO_2 increased 8–15 times the rate of CO_2 interaction with surfaces.

The simultaneous formation of isobutylene and synthesis gas upon interaction of isobutane with CO_2 allows to propose a new process for the production of methyl-tert-butyl ether (MTBE)

$$i\text{-}C_4H_{10} + CO_2 \rightarrow i\text{-}C_4H_8 + H_2O + CO$$

$$\rightarrow MTBE$$

$$\hookrightarrow CO + H_2 \rightarrow CH_3OH$$

5. Conversion of n-heptane

Heavy alkanes are subject mainly to oxidative cracking upon interaction with CO_2 over manganese oxide catalysts. The reaction $n\text{-}C_7H_{16} + CO_2$ was studied on the K–Mn–O/Al_2O_3, La–Mn–O/Al_2O_3 and La–Mn–O/NaY catalysts at 540–670°C [10]. La–Mn–O/Al_2O_3 was the most active in CO_2 activation. CO and H_2 are formed over La–Mn–O/Al_2O_3 and K–Mn–O/Al_2O_3 in equal amounts.

The rate of CO formation in the reaction (1) was somewhat lower than the rate of CO formation in the reaction $C_7H_{16} + CO_2$. The rate of CO formation in the steady state conditions was 14 times higher than in conditions of the catalyst reoxidation. This means that the oxidation of the catalyst takes place.

$$MnO + CO_2 \rightleftharpoons MnCO_3 \qquad (21)$$

$$3MnCO_3 \rightleftharpoons Mn_3O_4 + CO + CO_2 \qquad (22)$$

The oxidative cracking of n-heptane upon interaction with CO_2 can be described by the general equations

$$C_7H_{16} \rightarrow C_4H_8 + C_3H_6 + H_2$$

$$C_7H_{16} \rightarrow 3C_2H_4 + C + 2H_2$$

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

$$C + CO_2 \rightleftharpoons 2CO \qquad (23)$$

6. Conclusion

The results described above obtained during the investigation of the reaction of C_1–C_7 alkanes with CO_2 on oxide catalysts show different mechanisms for lower and higher alkanes. The reaction $RH+CO_2$ proceeds by redox mechanisms, but CO_2 activation can take place in direct interaction with the reduced oxide or in the formation of intermediate complexes, or in CO_2 interaction with coke at the surface.

Oxygen removal from the catalyst in the case of CH_4 proceeds by direct interaction of the catalyst with the hydrocarbon. The CH_4 molecule in split into $C_{adc}+4H_{adc}$ (or $2H_2$).

In the case of C_2H_6 and C_3H_8 the oxygen removal takes place as a result of the catalyst interaction both with C_nH_m and with H_2 split from the alkane molecule.

At $C \geq 4$ direct dehydrogenation with subsequent hydrogen oxidation by H_2 prevails. At $C \geq 6$ the oxidative function of the catalyst leads also to coke oxidation with CO_2 participation.

The indispensable requirement is the selection of a system which absorbs and activates CO_2. The acidic properties of CO_2 necessitate the choice of a catalyst with basic properties. But alkaline and alkaline earth oxides are ineffective because of strong carbonate formation. Oxides of moderate basicity are necessary and moreover they must participate in a redox process with CO_2 reduction. Manganese oxides and possibly rare earth oxides satisfy this requirement.

7. References

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