

The regularities in the interaction of alkanes with CO₂ on oxide catalysts

O.V. Krylov ^a, A.Kh. Mamedov ^b, S.R. Mirzabekova ^b

^a *N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 117977, Russia*

^b *Yu.G. Mamedaliev Institute of Petrochemical Processes, Azerbaijan Academy of Sciences, ul. Telnova 30, Baku, Azerbaijan*

Abstract

Catalytic oxidation of C₁–C₇ alkanes by CO₂ 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 C₄–C₇ 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 CO₂ 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 CO₂ molecule can be used a non-traditional oxidant. The best reducing agent for CO₂ is hydrogen. It was shown [2] that methanol synthesis proceeds not by direct CO + H₂ interaction, but by preliminary CO transformation into CO₂



After that the interaction of CO₂ with H₂ gives methanol



But hydrogen is expensive. Hydrocarbons in the role of CO₂ reductants are more attractive.

The most intensively studied reaction of hydrocarbons with CO₂ is methane conversion into synthesis gas



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 C₁–C₇ interaction with CO₂ 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 C₂–C₇ 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.

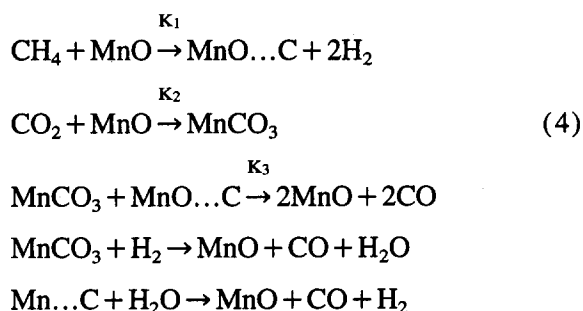
1. Methane conversion

The interaction of methane with CO₂ was studied on different oxide catalysts [7–9]. Under stationary conditions the 5%Ca–12%Mn–O/Al₂O₃

catalysts were the best ones. In the stationary state the reaction (3) of synthesis gas formation proceeds. At 930°C complete CO₂ and CH₄ consumption reaches 99.7% with CO selectivity and 84.6% with H₂ selectivity. The activity is stable

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:



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

$$r = \frac{k_1 P_{\text{CH}_4}}{1 + \frac{1}{k_2 k_3} \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} + k_2 P_{\text{CO}_2}} \quad (5)$$

where P_{CH_4} , P_{CO} , P_{CO_2} 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)



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



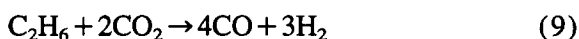
At 800°C ΔG for the reaction (7) is positive but not very high. The equilibrium yield of C_2H_6 at

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 , $V = 1800 \text{ hour}^{-1}$ and $\text{CH}_4/\text{CO}_2 = 5$ 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



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 , $V = 3600 \text{ hour}^{-1}$ and $\text{CO}:\text{C}_2\text{H}_6 = 1.5$. 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 $\text{C}_2\text{H}_6 + \text{CO}_2$ reaction proceeds non-selectively with formation of CO , H_2 and coke.

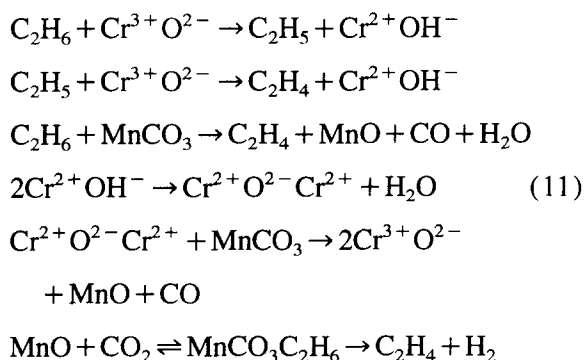
We have studied also the effect of modifying additions to Mn oxides of a series of oxides which are known as dehydrogenation catalysts (Sb, Zn, V, Fe, Cr oxides). The most active and selective catalyst for C_2H_4 production was found to be 5.5%Cr–17%Mn–O/ SiO_2 . Further increase of selectivity was observed 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)

$$r_{\text{C}_2\text{H}_4} = \frac{K_1 P_{\text{C}_2\text{H}_6} K_{\text{ox}} P_{\text{CO}_2}}{K_{\text{ox}} P_{\text{CO}_2} + K_{\text{red}} P_{\text{CO}}} \quad (10)$$

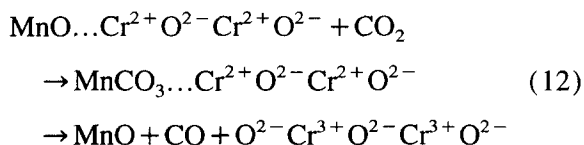
where K_{ox} and K_{red} are rate constants of the catalyst oxidation and reduction. The equation (10) describes the observed decrease of selectivity with conversion. This redox equation differs from the corresponding redox equation for alkane oxidation by oxygen where the denominator consists of the sum $K_{ox}P_{O_2} + K_{red}P_{C_nH_m}$.

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



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.

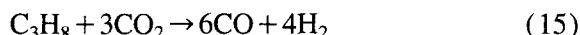
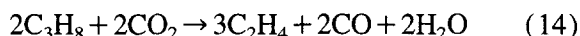


The chromium oxide phase is reduced and oxidized and the manganese oxide takes part in the reoxidation by CO_2 .

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



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

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

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

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

- [1] M. Aresta and G. Forti (Eds.), Carbon Dioxide as a Source of Carbon. Biochemical and Chemical Use, NATO ASI Ser., Ser. C, Reidel, Dordrecht, 1986.
- [2] A.Ya. Rozovskii and G.I. Lin, Theoretical Bases of Methanol Synthesis, Khimia, Moscow, 1990.
- [3] I.M. Bodrov and L.O. Apelbaum, Kinet. Katal., 8 (1969) 379.
- [4] J. Rostrup-Nielsen and J.H.B. Hansen, J. Catal., 144 (1993) 38.
- [5] A. Erdohelyi, J. Czerenyi and F. Solymosi, J. Catal., 141 (1993) 124.
- [6] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green and F.D.F. Vernon, Nature (London), 352 (1991) 225.
- [7] S.R. Mirzabekova, A.Kh. Mamedov, V.S. Aliev and O.V. Krylov, React. Kinet. Catal. Lett., 47 (1992) 159.
- [8] A.Kh. Mamedov, S.R. Mirzabekova, V.S. Aliev and O.V. Krylov, Kinet. Katal., 33 (1992) 591.
- [9] S.R. Mirzabekova, A.Kh. Mamedov and O.V. Krylov, Kinet. Katal., 34 (1993) 529.
- [10] A.Kh. Mamedov, P.A. Shiryayev, D.P. Shashkin and O.V. Krylov, Stud. Surf. Sci. Catal., 55 (1990) 477.