

in a 2:1 ratio. Purification by gas-liquid chromatography gave (IVa) as a pure compound. Found, %: C 66.53, H 7.22, N 25.86. $C_4H_8N_2$. Calculated, %: C 66.60, H 7.40, N 25.92.

Conclusions

The reaction of 2-methyl and 4(5)-methylimidazoles with acetylene in the presence of Cu_2Cl_2 leads to the corresponding N-vinyl derivatives. 1-Vinyl-4(5)-methylimidazole is formed as a mixture of two isomers differing in the position of the methyl group.

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MANGANESE CATALYSTS FOR THE OXIDATIVE CONDENSATION OF METHANE WITH ALKALI AND ALKALINE-EARTH METAL SALT ADDITIVES

Kh. M. Minachev, N. Ya. Usachev, Yu. S. Khodakov,
V. N. Udut, and P. A. Makarov

UDC 541.128:542.943.
7+542.953:547.211

The intensive search for catalysts for the conversion of methane to C_2 -hydrocarbons, which began with the work of Keller and Bhasin [1], has revealed the feasibility of the oxidative transformation of CH_4 to C_2H_6 and C_2H_4 in a series of oxide systems [2-11]. In our previous work [4, 5], we have shown that some manganese catalysts display significant activity and selectivity in these reactions. In order to increase the efficiency of such systems, we studied the modifying effect of alkali and alkaline-earth metal (M) salts, which, according to various workers [3, 6-8, 10, 11], enhance the selectivity of a number of catalysts.

Experimental

The catalysts studied were prepared by impregnation of KSK silica gel by a solution containing $Mn(NO_3)_2$ and M salts with subsequent evaporation and drying at $100^\circ C$ and roasting at $800^\circ C$ for 2 h. The content of Mn and M in all the catalysts contained 10 and 4 mass %, respectively. These experiments were carried out at $800^\circ C$. The CH_4 /air mole ratio was 0.55 and $v = 2000\ h^{-1}$. The experimental procedure and analysis of the reaction products were given in our previous work [4].

Results and Discussion

The introduction of alkali and alkaline-earth metals markedly alters the catalytic properties of the Mn/SiO_2 catalyst in the oxidative transformation of methane (Table 1). The total methane conversion (X) on manganese catalysts without additives M is 16.4% with 48.6% selectivity relative to C_2 -hydrocarbons (S), while these parameters in the presence of $(Mn-Na)/SiO_2$, rise to 23.9 and 70.5%, respectively. An increase in X is also found for the lithium additives, but there is a reduction in S. The addition of potassium and cesium salts decrease X but enhance S. The yield of C_2 -hydrocarbons is minimal on catalysts modified by magnesium and calcium salts (3.2-3.3%), which is a

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2124-2126, September, 1987. Original article submitted December 2, 1986.

TABLE 1. Catalytic Properties of Manganese Catalysts with Added Alkali and Alkaline-Earth Acetates in the Oxidative Condensation of Methane

M	X, %		S, %	[C ₂ H ₄]/[C ₂ H ₆] mole ratio
	total	C ₂ H ₄ +C ₂ H ₆		
—	16,4	8,0	48,6	5,7
Li	25,4	11,1	43,5	1,9
Na	23,9	16,9	70,5	20,1
K	11,3	7,2	63,4	3,5
Cs	11,2	6,0	53,4	2,8
Mg	11,5	3,2	27,6	1,3
Ca	13,5	3,3	23,9	1,2

TABLE 2. Effect of the Nature of the Anion of the Sodium Salt on the Catalytic Properties of (Mn-Na)/SiO₂ Catalysts in the Oxidative Condensation of Methane

Salt	X, %		S, %	[C ₂ H ₄]/[C ₂ H ₆] mole ratio
	total	to C ₂ H ₄ +C ₂ H ₆		
CH ₃ COONa	23,9	16,9	70,5	20,1
NaF	22,3	9,8	43,9	2,9
NaCl	33,3	25,8	77,5	17,4
NaBr	26,8	19,2	71,6	26,4

result of a reduction in both X and S. The very high content of C₂H₄ in the case of the Mn-Na catalyst (95%) is striking. The other catalysts are markedly inferior to the Mn-Na sample relative to this parameter (see Table 1).

The decomposition of the starting metal acetates under the conditions of the prior treatment of the catalyst likely leads to more stable carbonate salts. In order to elucidate the effect of the nature of the anion of the M salt, we tested (Mn-Na)/SiO₂ catalysts prepared using sodium halides (Table 2).

The sample with added NaF is not less active than the catalyst with sodium acetate but has a lower S value (43.9%), which makes it comparable in C₂-hydrocarbon yield with the unmodified manganese sample (see Table 1). The sharp increase in the yield of C₂-hydrocarbons to 25.8% is found on the catalyst with NaCl due to enhanced X and S. The (Mn-NaBr)/SiO₂ sample occupies an intermediate position relative to efficiency. We should note that the C₂-hydrocarbon product formed on all the sodium-containing catalysts with the exception of the catalyst with NaF consist of ≥95% ethylene (see Table 2).

These results indicate that the addition of sodium salts to Mn/SiO₂ catalysts significantly improves its catalytic properties in the oxidative condensation of methane. As proposed by Ito et al. [6], who studied the promotion effect of lithium on MgO, the conversion of CH₄ begins with the abstraction of a hydrogen atom and the formation of methyl radicals, which then recombine to give ethane. The first step is the most difficult and proceeds with the participation of Li⁺O⁻ sites [6]. In the case of the manganese systems, oxygen with enhanced reactivity is likely a component of the active sites, whose formation and properties are affected by the addition of alkali and alkaline-earth metals. In turn, the modifying effect of M depends on the nature of the anions interacting with Mn⁺. According to Otsuka et al. [10], the LiCl-Sm₂O₃ catalyst displays greatest selectivity relative to ethylene formation among Sm₂O₃ catalysts promoted by lithium salts. These authors assumed that the effect of chloride ions is a consequence of the inhibition of the extensive oxidation of methane and the hydrocarbons formed. The enhanced activity of Mn/SiO₂ with added NaCl observed in our work should not be attributed only to suppression of extensive hydrocarbon oxidation. Chloro derivatives of methane, which participate in the oxidative condensation of methane, may be formed under the reaction conditions on this catalyst.

Conclusions

1. The addition of acetates of alkali (Li, Na, K, and Cs) and alkaline-earth (Mg and Ca) metals affects the catalytic properties of Mn/SiO₂ catalysts in the oxidation condensation of methane to give C₂-hydrocarbons.
2. The promotion effect of sodium salts depends on the nature of the salt anion. Greatest efficiency is found for the (Mn + NaCl)/SiO₂ catalyst. At 800°C and methane/air mole ratio equal to 0.55, C₂-hydrocarbons are formed on this catalyst with 25.8% yield and 77.5% selectivity; the ethylene content in the methane condensation products is 95%.

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FEASIBILITY OF A QUANTITATIVE DESCRIPTION OF HALIDE ANION ABSTRACTION FROM AROMATIC RADICAL-ANIONS USING QUANTUM CHEMICAL REACTIVITY INDICES

A. I. Rusakov, A. S. Mendkovich, V. N. Leibzon,
G. S. Mironov, and V. P. Gul'tyai

UDC 530.145:541.42:
541.127:542.944.7

Considerable work has been devoted to the theoretical description of the dissociation of the carbon-halogen bond in radical-anions (RA) of organic halides [1-6].



In particular, there have been attempts to establish a correlation between the observed experimental rate constants k_1 of this process and the electronic structure parameters of the corresponding RA [1-4, 6]. However, the use of standard reactivity indices (RI) such as spin density, the reaction site (RS), and the energy and structure of the RA frontier orbitals provides satisfactory results only on a qualitative level [1-3] or only for a rather narrow class of related compounds [4]. A sufficiently broad range of halides was examined only by Andrieux et al. [6], who took the experimental equilibrium potential E^0 as the RI. Unfortunately, the correlation of $\log k_1$ with E^0 , according to these workers, is more qualitative than quantitative in nature.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2127-2129, September, 1987. Original article submitted December 17, 1986.