Rh – NaX AS A HETEROGENEOUS CATALYST FOR THE SYNTHESIS OF METHYL ACETATE BY THE CARBONYLATION OF METHANOL WITH CARBON MONOXIDE AT ATMOSPHERIC PRESSURE

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The synthesis of CH_3COOH and its derivatives from CH_3OH and CO has great practical importance in connection with the expanding volume of its use. Recently [1] a method was developed for the liquid-phase carbonylation of CH_3OH with carbon monoxide using $RhCl_3$ and rhodium complexes as the homogeneous catalysts, which were characterized by a high selectivity at a CH_3OH conversion exceeding 90%. The principal deficiencies of this process are the low output, and the complexity of separating and regenerating the catalyst. A heterogeneous catalyst of 3% Rh deposited on activated carbon was proposed, which has a high activity at 220-250° and a CO pressure of 10 atm. At atmospheric pressure the CH_3OH conversion to CH_3COOCH_3 did not exceed 50%, while the output of the catalyst was 8-18 g of acetate/g of Rh · h [2, 3].

We found that the Rh–NaX catalyst, prepared by impregnating zeolite with aqueous $RhCl_3$ solution and containing ~0.2% of Rh, is highly active, stable, and highly efficient in the carbonylation of CH_3OH with carbon monoxide at 250° and atmospheric pressure (Table 1). When methanol, containing 5-10 mole % of CH_3I, was passed through at a space velocity of 0.63 h^{-1}, and $CH_3OH:CO = 1.4\text{-}2.0$, the CH_3OH conversion was ~79%, while the selectivity in methyl acetate was 87-90%. The sole side product was dimethyl ether. The output of the catalyst was 46-52 g of acetate/g of Rh · h, i.e., it exceeded by 3-5 times the output of the known heterogeneous Rh catalysts. The carbonylation of CH_3OH fails to proceed in the absence of CH_3I, which indicates it to be an astoichiometric component [4]. The reaction does not go in the presence of the NaX and NaA zeolites without the Rh.

TABLE 1. Carbonylation of CH_3OH in Presence of Rh–NaX Catalyst (p_{CO} 1 atm, 250°C, space velocity of CH_3OH 0.63 h^{-1})

Amount		CH_3OH conversion, %	Yield, in % of CH_3OH passed through		Output, g of acetate/g of Rh · h	Composition of catalyzate, *%			
Rh, % (in catalyst)	CH_3I, mole % (in CH_3OH)		CH_3COOCH_3	CH_3OCH_3		CH_3OCH_3	CH_3I	CH_3COOCH_3	CH_3OH
0,25	5	52,5	46,4	10,3	45,6	11,3	19,3	52,4	17,0
0,25	10	78,6	55,8	13,0	52,2	10,3	35,5	45,0	9,2
1,00	10	47,6	40,0	8,6	10,6	7,5	31,4	35,1	26,0
1,00	20	71,0	68,5	8,8	13,1	4,7	58,7	32,0	4,6
1,00	30	94,0	71,5	10,0	13,2	3,8	67,0	27,0	22,0

*The catalyzate composition was determined by gas–liquid chromatography on an LCM-8MD chromatograph (column length 3 m, 15% polyethylene glycol 15,000 deposited on Chromosorb W (30-60 mesh), carrier gas = helium, and He flow rate = 40 ml/min).

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