Synthesis of Acetic Acid from Methanol and Carbon Monoxide on Nickel-based Catalysts supported on Active Carbon

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Summary Vapour-phase carbonylation of methanol to acetic acid with high yield and selectivity has been achieved by using nickel-based catalysts supported on active carbon under atmospheric pressure at *ca.* 310 °C.

Synthesis of acetic acid from methanol and carbon monoxide has been carried out commercially using a rhodium catalyst with methyl iodide as promoter.[1] Attempts to find an alternative catalyst because of the limited resources and extremely high cost of rhodium have met with only limited success.[2]

We report here a novel catalyst system which could possibly replace conventional rhodium catalysts. We have already found that Ni-based composite catalysts such as Ni–La_2O_3–Ru have a high activity for methanation of carbon monoxide[3] and direct hydrogenation of active carbon.[4] It was confirmed that the composite catalyst more readily adsorbs carbon monoxide than a nickel catalyst[5] and it adsorbs methanol more strongly than carbon monoxide.[6] These results suggested the possibility of high activity for the carbonylation of methanol. Indeed, use of the composite catalyst led to the formation of only a small amount of acetic acid ($0{\cdot}003$ mol dm^{-3} h^{-1}), in the absence of organic halogen compounds such as methyl iodide. Introduction of methyl iodide into the reaction gas stream led to a good yield of acetic acid.

Table. Yields of products for various catalysts.

	1·0% Ni	5·0% Ni	10·0% Ni	5·0% Ni–2·8% La_2O_3	4·8% Ni–2·5% La_2O_3–1·2% Ru	1·0% Ni (as $NiCl_2$)	2·0% Rh
Temperature[a]/°C	320	320	320	320	300	320	280
Apparent methanol conversion[b]/%	62·8	56·7	103[c]	80·5	74·0	77·8	68·5
Yield/mol dm^{-3} h^{-1}							
$MeCO_2H$	2·00	2·17	3·93	3·32	2·44	2·56	1·68
$MeCO_2Me$	0·44	0·16	0·19	0·16	0·50	0·55	0·82
Me_2O	0·04	0·02	0·04	0·04	0·04	0·04	0·03
CH_4	0·36	0·45	1·11	0·56	0·39	0·43	0·28

[a] The temperature at which the maximum yield of acetic acid was obtained. [b] Calculated from the initial amount of the methanol. [c] Methyl iodide in the reactant gas may contribute to the $>100\%$ conversion.

A normal active carbon (30—60 mesh, Shimadzu Seisakusho Co. Ltd.) was used as the catalyst support. It had a B.E.T. surface area of 1230 m^2 g^{-1} and a porosity of 0·46. Catalysts were prepared by the impregnation method according to the procedure reported previously,[4] and packed in a continuous flow reactor with an inside diameter of 8 mm. The reaction gas mixture, composed of 17 mol% of methanol, 66 mol% of CO, 2·5 mol% of methyl iodide, and 14 mol% of N_2, was introduced to a 2 cm^3 (1 g) portion of catalyst under atmospheric pressure. The space velocity of the gas was kept at 700 h^{-1}. The reaction temperature was varied from 260 to 360 °C.

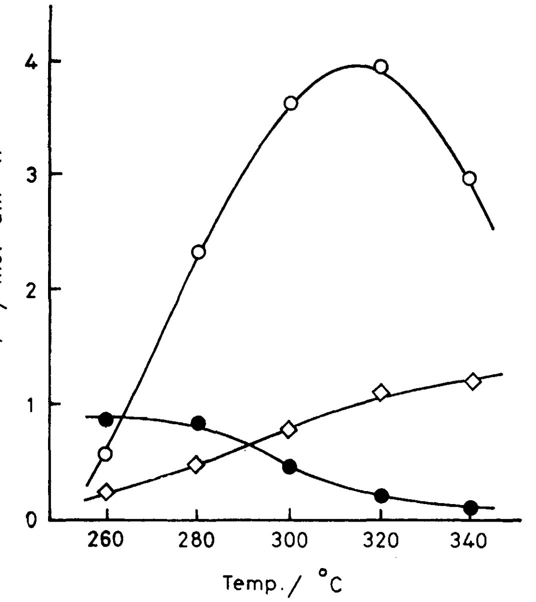

Figure. Effect of temperature on space-time yields (Y^{ST}) of products of methanol carbonylation on the 10% Ni catalyst. (○) Acetic acid; (●) methyl acetate; (◇) methane.

An example of the temperature dependence of the space-time yield of each product in the case of one of the nickel catalysts is shown in the Figure, which shows that acetic acid was the main product. The yield of acetic acid increased with reaction temperature up to *ca.* 310 °C and then decreased. Considerable amounts of methyl acetate were formed below 300 °C, but amounts decreased above that temperature with increase in formation of methane. Dimethyl ether and hydrogen were formed as by-products, but in yields of $<0{\cdot}053$ and 0·029 mol dm^{-3} h^{-1}, respectively.

A comparison of the performance of various catalysts is surveyed in the Table. The yield of acetic acid increased with the nickel content of the catalyst, and catalyst activity was maintained at least for 28 h in the case of the nickel catalysts. Combination of small amounts of La_2O_3 or La_2O_3–Ru with the nickel increased the activity, but the activity then decreased gradually with reaction time. It is noteworthy that the reduced nickel catalyst may be replaced by nickel chloride. The rhodium catalyst exhibited an activity at lower temperatures comparable with that of the nickel catalysts, but selectivity for acetic acid formation was low and the yield of acetic acid decreased above 280 °C.

These results show the potential for the use of nickel-based catalysts supported on active carbon as a replacement for rhodium catalysts.

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