

Liquid phase methanol carbonylation catalysed over rhodium supported on hydrotalcite

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A solid catalyst, Mg–Al hydrotalcite containing nanometer size rhodium particles, is active for liquid phase methanol carbonylation to methyl acetate at 473 K in the presence of methyl iodide.

Acetic acid and methyl acetate are industrially synthesised by carbonylation of methanol with a homogeneous rhodium catalyst promoted by methyl iodide.^{1,2} Attempts have been made to use heterogeneous catalysts for methanol carbonylation,^{3,4} because such a system would be advantageous in separation and recovery of the products and recycling of the catalyst, providing greater economic advantages and minimizing the environmental impact of the process. A number of supported rhodium systems such as zeolites,^{5,6} polymers,⁷ activated carbon⁸ and inorganic oxides⁹ are reported to be active under vapour phase conditions. In the liquid phase, polymer supported Rh(I) catalysts have been reported,¹⁰ however, this system is unstable due to loss of rhodium.

Hydrotalcite, $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_{x/2}\cdot y\text{H}_2\text{O}]$, consists of positively charged brucite-like layers with charge-balancing anions and water molecules.¹¹ The material shows strong basicity and is often employed as a precursor for catalysts or catalyst supports owing to its structure.¹² In the present work, we have demonstrated that nanometer size rhodium particles can be stabilized on hydrotalcite and the solid effectively catalyses the liquid phase carbonylation of methanol in the presence of methyl iodide. This may provide a realistic solution to problems such as separation, recovery, *etc.* associated with homogeneous catalytic systems.

An Mg–Al hydrotalcite (Mg/Al = 2/1) was synthesised using the procedure reported by Reichle.¹³ Rhodium was loaded on the Mg–Al hydrotalcite by a deposition–precipitation method. In a typical procedure, Mg–Al hydrotalcite was placed in an aqueous solution of $\text{Rh}(\text{NO}_3)_3$ (Kanto Chemical) at 343 K and an aqueous solution of Na_2CO_3 (1 M) was added dropwise. The pH of the solution was kept at 10 for 1 h. The resulting solid was filtered off and washed thoroughly with distilled water, dried and then calcined in air at 673 K for 4 h. A rhodium catalyst was also prepared by the impregnation technique. After evaporation of a mixture of the solution of $\text{Rh}(\text{NO}_3)_3$ and hydrotalcite, the wet solid was dried and calcined in air at 673 K for 4 h. The Rh contents in the samples was analysed by ICP emission spectrometry.

Adsorption experiments were performed with a vacuum system equipped with Baratron vacuum gauges after the samples were reduced with hydrogen at 673 K for 2 h. The BET surface areas of the samples were determined from nitrogen physisorption isotherms.

Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku Rotaflex 20 diffractometer using nickel-filtered Cu-K α (40 kV, 150 mA) radiation.

Catalytic tests were performed in an autoclave (0.2 dm³). Prior to the reaction, the catalyst (0.20 g) was activated under evacuation followed by reduction with hydrogen at 673 K for 2

h and sealed in a glass capsule. The capsule was placed in the reactor along with a mixture of methanol (780 mmol) and methyl iodide (35 mmol), and CO was introduced at 0.5 MPa (42 mmol) after displacing air inside the reactor with argon. The capsule was broken during pressurization and the reactor was heated to 473 K. The products were analysed with an Ohkura-802 gas chromatograph (TCD) with PEG 1500 (2 m) and Poropak T (2 m) columns.

The powder XRD pattern of the parent hydrotalcite confirmed that the sample was well crystallised, but broadening of the peaks was observed for the hydrotalcite containing rhodium (Fig. 1). A change in the BET surface area after modification with rhodium was also observed. The surface area decreased with an increase in the rhodium content for the hydrotalcite with an original surface area of 232 m² g⁻¹ (Table 1). The surface area of the sample prepared by the impregnation method was very small in comparison with the samples prepared by deposition–precipitation.

Carbon monoxide was adsorbed on the samples containing rhodium reduced at 673 K. The amount of carbon monoxide adsorbed was saturated at *ca.* 1 kPa. On the basis of the amounts saturated, the surface areas of rhodium in the samples were tentatively calculated, assuming atomic adsorption of CO on a

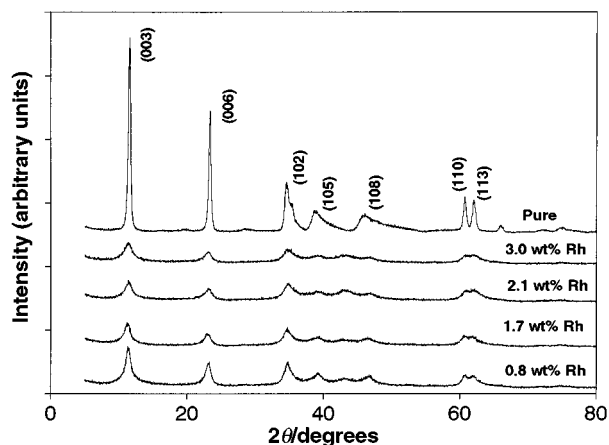


Fig. 1 XRD patterns of hydrotalcite modified with rhodium by deposition–precipitation.

Table 1 Some surface properties of Rh/Mg–Al hydrotalcite catalysts prepared by the deposition–precipitation method

Rhodium content (wt%)	BET surface area/m ² g ⁻¹	CO uptake/($\mu\text{mol g}^{-1}$)	Rhodium surface area/m ² g ⁻¹
0.8	159	n.d. ^a	n.d.
1.7	116	44	1.5
2.1	104	50	1.7
3.0	86	39	1.3
1.5 ^b	80	18	0.6

^a Not determined. ^b Prepared by impregnation.

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Table 2 Methanol carbonylation over Rh/Mg–Al hydrotalcite catalysts at 473 K for 4 h

Rhodium content (wt %)	MeOH conversion (%)	Products/mmol		
		MeCHO	MeOAc	DME
0.8	12.7	0.1	21	29
1.7	16.3	0.2	30	33
1.7 ^a	5.8	0.1	2	20
2.1	16.2	0.5	32	31
3.0	15.0	0.3	23	35
1.5 ^b	7.7	0.2	9	21

^a Reaction time = 1 h. ^b Prepared by impregnation.

rhodium site and a site density of 0.058 nm² (Table 1). The mean particle sizes of rhodium were calculated from the data in Table 1 assuming that all the rhodium particles are spherical and on the surface, and gave values of 5, 6 and 11 nm, respectively, for deposition–precipitation samples containing 1.7, 2.1 and 3.0 wt% of rhodium. The Rh particle size for the sample prepared by the impregnation method (1.5 wt% of Rh) was calculated as 12 nm. Particles of > 10 nm are expected to be large enough to enable detection by XRD. However, no peaks attributed to rhodium metal were evident in the patterns of any of the samples after reduction, with the XRD patterns being similar to those of Fig. 1. Since the stoichiometry of the adsorption varies with the chemisorption mode of CO (for bridge-type adsorption a CO molecule occupies two rhodium sites), the rhodium surface areas in Table 1 may be underestimates and would result in larger particle sizes. Hence, the actual particle sizes of rhodium may well be smaller than the values estimated by adsorption of carbon monoxide. The reduction of the BET surface area after modification of rhodium suggests that some of the rhodium particles are incorporated in the bulk phase of the hydrotalcite and so will be another reason for the apparent contradiction of the adsorption and XRD results.

Mg–Al hydrotalcites containing rhodium were found to be active for methanol carbonylation at 473 K. The main products were methyl acetate (MeOAc) and dimethyl ether (DME) with a small amount of acetaldehyde (Table 2). Neither acetic acid, nor other decomposition products such as hydrogen were detected. Loss of methyl iodide was not observed and no trace of rhodium was detected in the liquid phase after the reaction. The XRD patterns of the catalyst recovered after the reaction were very similar to those prior to the reactions, showing that the catalysts retain the hydrotalcite structure during reaction. No reaction products were obtained with rhodium-free Mg–Al hydrotalcite. An increase in rhodium content to 2.1 wt% enhanced formation of MeOAc while a further increase of rhodium to 3.0 wt% resulted in a lower yield of MeOAc. The catalyst prepared by the impregnation method with a rhodium content of 1.5 wt% was the least active. The activity towards MeOAc mainly depends on the estimated surface area of rhodium (*cf.* Tables 1 and 2).

No methanol carbonylation occurred in the absence of methyl iodide for the catalyst containing 1.7 wt% of rhodium except for

formation of a small amount of DME. Hence, methanol cannot be directly carbonylated over the catalyst, and the presence of methyl iodide is essential in the carbonylation. This suggests that carbonylation of methyl iodide to acetyl iodide is a key step of the carbonylation as also found for homogeneous carbonylation with rhodium complexes.¹⁴ Formation of MeOAc was low after reaction for 1 h with the catalyst containing 1.7 wt% of Rh while DME formation was considerable (Table 2). This result indicates an induction period for the formation of MeOAc. Formation of homogeneous rhodium species during the induction period might be possible. However, no acetic acid, which is one of the major products in homogeneous carbonylation,² was detected in the reaction with the heterogeneous catalyst. In the mechanism for homogeneous carbonylation, methyl acetate is formed as a product of a subsequent esterification of acetic acid and methanol.² The product distribution with the heterogeneous catalyst is similar to that found for the vapour phase carbonylation of methanol in the presence of methyl iodide over rhodium supported on activated carbon⁸ while methyl acetate appears to be directly produced in the reactions. The similarity suggests that the carbonylation with rhodium containing hydrotalcite takes place on the surface of rhodium particles. Carbonylation of DME to MeOAc has been proposed in the vapour phase reaction, and can account the selective formation of MeOAc and the induction period.¹⁵

In summary, nanometer sized rhodium particles can be stabilised on hydrotalcite, and methyl acetate is directly formed in the liquid-phase methanol carbonylation with supported rhodium catalysts. A detailed kinetic study is in progress, which should provide stimulating results for practical modifications of the methanol carbonylation process.

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