

Nickel-catalysed Isomerization of Methyl Formate to Acetic Acid

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The rate of isomerization of methyl formate to acetic acid on a nickel catalyst has been greatly increased to a level comparable with that on a rhodium catalyst by using a trialkylamine, a tetra-alkyltin, and hydrogen as promoters.

The potential for methyl formate as a building block in the synthesis of various chemicals is based on its unique position in C_1 chemistry.¹ The synthesis of methyl formate from CO and methanol is an established, commercial technology. The fact that methyl formate can easily be decomposed at temperatures lower than 200 °C, by using an appropriate catalyst of fixed bed type, to methanol and CO dictates its various applications as a CO carrier. The CO and methanol thus produced can be used for synthesis of acetic acid.

Without dissociation, methyl formate can also be directly isomerized to acetic acid *via* an alternative route. Depending on the source of carbon monoxide, the synthesis of acetic acid by isomerization of methyl formate can compete favourably with methanol carbonylation. Satisfactory yields have been obtained using transition metal (Rh,^{2–4} Ir,⁵ Co,⁶ Ni,⁷ Ru,^{8–9} or Pd^{8–9}) complex catalysts, and an iodide promoter. Ni is less active than Rh or Ir, but has excellent selectivity for formation of acetic acid when an organic nitrogen compound is employed as an additional promoter. The high selectivity for acetic acid, rivalling that of the Rh-based chemistry, will allow the use of inexpensive, non-noble metal as an alternative to expensive noble metal catalysts. The most significant problem in using Ni

as a catalyst for acetic acid synthesis is the low turnover rate⁷ (14 h⁻¹) compared to Rh^{4,9} (200–400 h⁻¹) [turnover rate/h⁻¹ = (mol acetic acid)/(mol transition metal h)], and the requirement for a high iodide content (20 wt%).

Recently we have found that a catalyst system involving Ni as a catalyst and trialkylamine, tetra-alkyltin, and hydrogen as promoters shows high activity in the isomerization of methyl formate to acetic acid in the temperature range 140–220 °C, and the pressure range 10–50 bar of CO and 1.4–10 bar of H₂. Acetic acid synthesis can be carried out efficiently by adding a catalytic amount of Ni powder, methyl iodide, and various amounts of promoters to methyl formate (50 ml) in acetic acid solvent (50 ml) in an Autoclave Engineers 300 ml Hastelloy-C autoclave equipped with a temperature controller. After being purged with 14 bar of CO several times, the reactor was pressured to 10–50 bar with CO and heated to the desired temperature with stirring (500 rpm). After the required time, the liquid phase was sampled and analysed by a

Table 1. Effect of Sn compounds on the isomerization of HCO₂Me catalysed by the Ni/MeI/NR₃ system in MeCO₂H at 180 °C and 30 bar of CO.^a

[SnBu ₄]/mM	% HCO ₂ Me converted	% Selectivity		
		HCO ₂ H	MeCO ₂ Me	MeCO ₂ H
0	53	13	29	58
2.4	53	8	29	63
3.8	54	7	28	65
6.2	67	6	27	67
25	88	6	9	85
50	89	4	6	90
50 ^b	81	3	6	91

^a [Ni] = 0.07 M, [HCO₂Me] = 6.6 M, [MeI] = 1.6 M, [NBu₃] = 0.34 M, *t* = 1 h after increasing temperature to 180 °C. ^b SnCl₂ was used; conditions similar otherwise.

Table 2. Addition of SnR₄ to a Ni/MeI/NR₃ system in MeCO₂H at 180 °C and 30 bar of CO.^a

[NBu ₃]/M	[Sn(C ₃ H ₁₁) ₄]/M	Initial turnover rate/h ⁻¹
0.34	—	43
0.34	0.042	86
—	0.042	30

^a As in Table 1 except [NBu₃] is varied.

Table 3. Effect of hydrogen partial pressure on the isomerization of HCO₂Me catalysed by the Ni/MeI/NR₃/SnR₄ system in MeCO₂H at 180 °C and 30 bar initial CO partial pressure.^a

H ₂ partial press./bar	% HCO ₂ Me converted	% Selectivity		
		HCO ₂ H	MeCO ₂ Me	MeCO ₂ H
0	53	8	29	63
1.4	62	0	31	69
5	69	0	27	73
10	63	7	28	65

^a As in Table 1 except [SnBu₄] = 2.4 mM.

Table 4. Comparison of catalytic systems for the isomerization of HCO_2Me to MeCO_2H .

Catalyst	CO pressure /bar	$T/^\circ\text{C}$	Wt% of iodide	Turnover rate/ h^{-1}	Ref.
$\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{MeI}$	15	200	4	448	3
$\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{LiI}$	28	180	10	313	4
$\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{MeI}$	33	200	3	235	9
$[\text{Ir}(\text{COD})\text{Cl}]_2/\text{MeI}^{\text{a}}$	1	190	8	338	5
$\text{IrCl}_3 \cdot 3.5\text{H}_2\text{O}/\text{MeI}$	70	235	3	500	9
$\text{Ni}/\text{MeI}/2,6\text{-lutidine}^{\text{b}}$	10	180	12	14	7
$\text{Ni}/\text{MeI}/\text{NBu}_3/\text{SnBu}_4^{\text{c}}$	30	180	16	237	^d

^a In EtCO_2H solvent; COD = cyclo-octadiene. ^b In $\text{PhCOMe}-\text{MeCO}_2\text{Me}$ solvent. ^c In MeCO_2H solvent. ^d Our work.

Perkin-Elmer gas chromatograph with a thermal conductivity detector.

Starting with a $\text{Ni}/\text{MeI}/\text{NR}_3$ system we added various proportions of SnR_4 . The promotion ability of tetra-alkyltin reagents (Table 1), in terms of both activity and selectivity, increases as its concentration increases in the range of concentration examined. The turnover rate obtained here, 81 h^{-1} , is considerably higher than previously reported using Ni and organonitrogen compounds.⁷ Systems using a tetra-alkyltin as a cocatalyst, especially with Ni as a catalyst, are rare. SnR_4 is a more efficient promoter than SnCl_2 in our system (Table 1). Exceptionally high selectivity was obtained for formation of MeCO_2H and MeCO_2Me in all our experiments.

Starting from a $\text{Ni}/\text{MeI}/\text{NR}_3$ system ($[\text{NR}_3]/[\text{Ni}] = 5$) we studied the influence of the addition of SnR_4 on the initial turnover rate (Table 2). When we added as little as 5 mmol of $\text{Sn}(\text{C}_5\text{H}_{11})_4$ to the 42 mmol of NBu_3 present, the initial rate was doubled. There is obviously a synergy between the two different promoters since the rate for the $\text{Ni}/\text{MeI}/\text{NBu}_3/\text{Sn}(\text{C}_5\text{H}_{11})_4$ system is much greater than the sum of the two rates independently obtained with the $\text{Ni}/\text{MeI}/\text{NBu}_3$ and $\text{Ni}/\text{MeI}/\text{Sn}(\text{C}_5\text{H}_{11})_4$ systems under otherwise identical conditions. The role of the tin compound is not yet clear, but the fact that trialkylamine and tetra-alkyltin show a significant synergistic effect suggests they somehow act together efficiently to activate the Ni catalysts. Their ratio was not optimized.

The effect of hydrogen partial pressure on activity and selectivity in Ni-catalysed isomerization of methyl formate is shown in Table 3. An increase in activity and selectivity occurs on increasing the H_2 partial pressure to ca. 5 bar, whereas H_2 partial pressures above 5 bar appear to be

detrimental to activity and selectivity. With the exception of traces of methane, no other hydrogenation product was formed. This activation by hydrogen is significant, since syngas or carbon monoxide contaminated with a large amount of hydrogen is cheaper than pure carbon monoxide.

The best result obtained so far is a turnover rate of 237 h^{-1} at 180°C and 30 bar of CO with $[\text{Ni}] = 0.035 \text{ M}$ and $[\text{SnBu}_4] = 0.05 \text{ M}$. Although this catalyst system shows a reaction rate in the $43\text{--}237 \text{ h}^{-1}$ range, which is slightly inferior to the current best results with rhodium, it shows significant improvement over other Ni-catalysed isomerization systems (Table 4). With optimization of reaction conditions, there should be room for improvement. Therefore, considering the high price and scarcity of rhodium, these results are promising for the use of Ni as an alternative to rhodium.

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