Supporting Information:
Nickel catalyst stability towards carboxylic acids

Andrew D. Pienaar and Arno de Klerk *

Fischer-Tropsch Refinery Catalysis, Sasol Technology Research and Development,

P.O. Box 1, Sasolburg 1947, South Africa.

Tel: +27 16 960-2549, Fax: +27 11 522-3517, E-mail: arno.deklerk@sasol.com

Synthesis of nickel carboxylates

Materials. Sodium hydroxide (>97%) was supplied by CJ Chemicals, South Africa. The other chemicals were all supplied by Aldrich: nickel(ii) nitrate hexahydrate, ethanol (>99%), propanoic acid (>99%), butanoic acid (>99%) and pentanoic acid (>98%).

Synthesis. The C_3–C_5 nickel carboxylate species used in this study were synthesised by dropwise adding the relevant carboxylic acid to an aqueous slurry of the nickel(ii) hydroxide. The remaining solids were removed by centrifuging the solution before the nickel carboxylate was recovered by drying in a rotating evaporator. The nickel(ii) hydroxide that was used in the synthesis was prepared by adding sodium hydroxide to an aqueous solution of nickel(ii) and collecting the precipitate. Successful synthesis of nickel propanoate, nickel butanoate and nickel pentanoate was confirmed by infrared spectrometry (Table S1).[1]

Leaching procedures and experiments

Low temperature leaching. Low temperature catalyst leaching was performed in standard laboratory glassware. A round bottom flask was connected to a water cooler and heated by a heating mantle. A solution of propanoic acid in ethanol (1 M) was prepared and added to the catalyst to give a stoichiometric ratio of acid to nickel. Leaching was allowed to take place while stirring the mixture under reflux conditions for 24 hours. The spent catalyst was separated from the leaching solution in a centrifuge and dried in an oven at 100°C for 2½ hours. The leached product was obtained by concentrating the solution in a rotating evaporator and drying the solid overnight at ambient conditions. All products were analysed by infrared spectrometry.

Elemental analysis showed that nickel was not the only metal being leached, but that some of the aluminium of the support had been leached too. The carboxylate group's characteristic asymmetrical and symmetrical stretching bands[2] were observed in the infrared spectrum at 1575 and 1418 cm^{-1} (Table S2). These bands were broadened as would be expected from a mixture of carboxylates. A comparison of the infrared spectra of the fresh and leached catalyst after drying (Table S2) showed the appearance of narrow carboxylate absorption bands at 1549 and 1418 cm^{-1}. The C=O stretching at 1724 cm^{-1} is indicative of an aliphatic ketone or ester. This was quite surprising, since decomposition of the propanoic acid to yield 3-pentanone was not expected at such low temperature. It is more likely due to some ethyl propanoate formed by the leaching solution. This prompted a change in solvent.

High temperature leaching. High temperature catalyst leaching was performed in a stainless steel batch reactor with glass lining. Details of the experimental setup have been reported previously.[3] For each experiment the reactor was loaded with a mixture of catalyst (2 g) and solvent (distilled water, 120 g). The reactor was heated to the reaction temperature before propanoic acid (10 g) was introduced under pressure from a transfer vessel. The reaction was conducted at different temperatures (180-230°C) under 3.5 MPa nitrogen pressure to keep the carboxylic acid and solvent in the liquid phase. Catalyst leaching was monitored over time by taking samples at hourly intervals. The experiments were performed in triplicate to improve confidence in the results. The products were analysed by ultra violet-visible spectrometry.

The results of these experiments are reported in the manuscript.

Thermal behaviour of nickel carboxylates

The thermal behaviour of the C_2-C_5 nickel carboxylates that were reported in literature, is summarised in Table S3.[4-11]

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Literature cited

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Table S1. Infrared analysis of the synthesised nickel carboxylates showing the most prominent infrared absorption bands (cm^{-1}).

IR band assignment based on nickel propanoate[1]		nickel propanoate	nickel butanoate	nickel pentanoate
asymmetric C-H stretch of CH_3 (w)	2979	2974	2962	2957
asymmetric C-H stretch of CH_3 (s)	2942	2935	2929	2928
		2881	2872	2876
		1685	1681	-
asymmetric COO^- stretch (s)	1569	1562	1564	1545
asymmetric CH_3 deformation (m)	1467	1462	1466	1466
symmetric COO^- stretch (m)	1421	1401	1402	1407
symmetric CH_3 deformation (m)	1377	1375	1345	1359
CH_2 wag (s)	1309	1290	1308	1309
CH_2 twist (m)	1245	1245	1255	1232
		-	1214	1200
C^2-C^3 stretch (s)	1092	1080	1097	1109
C^1-C^2 stretch of complex (m)	988	1009	-	-
C^1-C^2 stretch (s)	895	886	897	929
CH_2 rock (w)	813	809	-	-

Table S2. Main infrared absorption bands (cm^{-1}) of the fresh catalyst, leached catalyst and leached product recovered from solution by evaporation of the solvent.

IR band assignment	Fresh catalyst	Leached catalyst	Leached product
O-H stretching	±3400 (very broad)	3380 (very broad)	3440 (broad)
C-H stretching of CH_3	-	2976 (very small)	2987-2890
C=O stretching	-	-	1724
	1635	±1630 (shoulder)	-
asymmetric COO^- stretching	-	1549	1575 (broad)
	1466 (broad)	1466	1475
symmetric COO^- stretching	-	1418	1418
	1382 (broad)	-	-
symmetric CH_3 deformation	-	1374	1375
CH_2 wagging	-	1300	1297
	-	1262	1229
C^2-C^3 stretching	-	-	1088
	1080 (shoulder)	1080	-
	1036	1033	-
C^1-C^2 stretching of complex	-	-	1011
	911	911	-
C^1-C^2 stretching	-	-	887
CH_2 rocking	-	-	814
	±800	800	-

Table S3. Thermal behaviour of nickel carboxylates in the temperature range 25-400°C under different environments as defined by the observed onset temperature. Heating in air resulted in oxidation before decomposition.

Compound	Loss of water (°C)	Decomposition (°C)	Environment	Reference
nickel ethanoate	60	260	Air	(4)
	80	220	Air	(5)
	68	284	Argon	(5)
	37	296	Vacuum	(5)
	95	160-230	Air	(8)
	80	275-300	Vacuum	(8)
	70-80	300-310	Air	(10)
	70-80	300-310	Helium	(10)
	90	315	Air	(11)
	95	280-300	Nitrogen	This work
nickel propanoate	-	214	Air	(5)
	-	240	Argon	(5)
	-	253	Vacuum	(5)
	70	285	Air	(9)
	-	280-290	Nitrogen	This work
nickel butanoate	-	280	Air	(4)
	40-50	278	Air	(6)
	40	283-297	Argon	(6)
	20-25	278	Vacuum	(6)
	-	305	Nitrogen	This work
nickel pentanoate	75	275	Air	(7)
	80-90	270-275	Argon	(7)
	80	265-270	Vacuum	(7)
	-	280-290	Nitrogen	This work