Selective hydrogenation of CO_2 gas to formic acid over nanostructured Ru-TiO_2 catalysts

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SUPPORTING INFORMATION

CO_2 loading on Ionic liquids [1-3]

In a typical procedure, the CO_2 capture was carried out in high pressure autoclave (100 mL). The absorbents were charged into the reactor at room temperature. Then, the air in the flask was replaced by passing CO_2. The absorption was conducted at 80°C with a 4 bar CO_2 gas for 1 hour. The amount of CO_2 absorbed was determined by calculating the weight of the reaction mixture with an analytical balance. Data points were taken with an accuracy of ±0.0001 g every five minutes. At 80°C slight while at 100°C complete desorption of CO_2 was recorded.

Table 4: Absorption study of CO_2 over ionic liquids

Ionic liquid	CO_2 pressure (bar)	Temperature (°C)	Time (h)	CO_2 Loading[1]
[mammim][NTf_2]	20	80	1	25
[mammim][TfO]	20	80	1	41
[mammim] [$CF_3CF_2CF_2CF_2SO_3$]	20	80	1	47
[mammim] [BF_4]	20	80	1	13
[DAMI][TfO]	20	80	1	51
[DAMI][NTf_2]	20	80	1	48
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	20	80	1	68
[DAMI][BF_4)	20	80	1	21
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	10	80	1	31
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	25	80	1	70
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	20	50	1	65
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	20	100	1	35
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	20	80	3	69
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	20	80	0.5	23

1. Moles of CO_2 captured per mole of ionic liquid

References:

1. Rahmana M H, Siajb M, Larachi F 2010 Chemical Engineering and Processing: Process Intensification 49 313.
2. Calleja E T, Skinner J,Tauste D G (2013) Journal of Chemistry 2013 1.
3. Yang Z-Z, He L-N (2014) Beilstein J. Org. Chem. 10 1959.

Analytical data of functionalized ionic liquids

[mammim][NTf_2]

^{1}H NMR (400MHz, $CDCl_3$): δ 2.17 (s, 6H), δ 2.52 (s, 3H), δ 2.71 (t, 2H), δ 3.59 (s, 3H), δ 4.17 (t, 2H), δ 7.25 (d, 1H), δ 7.28 (d, 1H). Positive ion HRMS (EI) m/z found: 426.2256 (calculated for $C_{17}H_{37}N_4O_4S_2$, M^+ requires: 426.2289).

[mammim] [$CF_3CF_2CF_2CF_2SO_3$]

^{1}H NMR (400MHz, MeOD): δ 2.15 (s, 6H), δ 2.55 (s, 3H), δ 2.31 (t, 2H), δ 3.62 (s, 3H), δ 4.19 (t, 2H), δ 7.23 (d, 1H), δ 7.30 (d, 1H). Positive ion HRMS (EI) m/z found: 468.1003 (calculated for $C_{13}H_{19}F_9N_3O_3S$, M^+ requires: 468.1002).

[mammim] [BF_4]

^{1}H NMR (400MHz, $CDCl_3$): δ 2.11 (s, 6H), δ 2.45 (s, 3H), δ 2.37 (t,2H), δ 3.65 (s, 3H), δ 4.22 (t, 2H), δ 7.28 (d, 1H), δ 7.35 (d, 1H). Positive ion HRMS (EI) m/z found: 265.1504 (calculated for $C_9H_{19}BF_4N_3$, M^+ requires: 256.1608).

[DAMI][$CF_3CF_2CF_2CF_2SO_3$]

^{1}H NMR (400 MHz, MeOD): d=2.58 (s, 12H), 2.82 (s, 3H), 2.89 (t, 4H), 4.49 (s, 4H), 7.71 ppm (d, 2H). Positive ion HRMS (EI) m/z found: 313.1663 (calculated for $C_{12}H_{26}BF_4N_4$, M^+ requires: 313.2181).

[DAMI] [BF_4]

^{1}H NMR (400 MHz, $CDCl_3$): d=2.48 (s, 12H), 2.79 (s, 3H), 2.85 (t, 4H), 4.42 (s, 4H), 7.70 ppm (d, 2H). Positive ion HRMS (EI) m/z found: 525.1542 (calculated for $C_{16}H_{26}F_9O_3S$, M^+ requires: 525.1580).

Catalyst poisoning experiments [1-3]

The mercury test has been widely applied to recognize the presence of heterogeneous catalysts as they have ability to poison metal (0) heterogeneous catalysts followed by formation of amalgam or adsorption on the metal surface. Mercury (0) is undoubtedly the most significant way of metal poisoning that form an amalgam. 5 equiv. Hg (0) was added before adding the reactants (CO_2 and H_2 gas) to the reaction mass (Table 6, entry-1 reaction condition was applied). The TON values of formic acid were reduced up to 28.5% (Table 2, entries 1) while no formic acid was formed, when we doubled the amount of Hg (0), theCO_2 hydrogenation reaction was completely inhibited (Table 2, entries 1 and 2). Since mercury has been testified to infrequently encourage the side reactions, the outcomes of the investigations are not always conclusive enough to know the catalyst nature. Therefore, to support our obtained results with Hg (0), we performed the second poisoning test with triphenyl phosphine (PPh_3) as they have a strong affinity to metal centers. If a catalyst is poisoned totally with <1 equiv. of PPh_3, such observation indicates the existence of a heterogeneous catalyst. The metal poisoning results with PPh_3 were summarized in table 2, entry 3 and 4. We observed that CO_2 hydrogenation reaction was completely inhibited either by stoichiometric or sub-stoichiometric quantity of PPh_3 (Table 2, entries 3-4).

Entry	Catalyst	Poison	Poison/ catalyst ratio (in equivalents)	TONx10^2 (mol_{FA}/mol_{Ru})
1	**1-Ru-TiO_2**	**Hg**	**5:1**	**38.1**
2	**1-Ru-TiO_2**	**Hg**	**10:1**	**0**
3	**1-Ru-TiO_2**	**PPh_3**	**1:1**	**0**
4	**1-Ru-TiO_2**	**PPh_3**	**0.5:1**	**0**

Reference:

1. J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem., 2003, 198, 317–341.
2. N.T.S. Phan,M. Van der Sluys, C.W. Jones, Adv. Synth. Catal., 2006, 348, 609–679.
3. Y. Lin, R. G. Finke, Inorg. Chem. 1994, 33, 4891 – 4910.

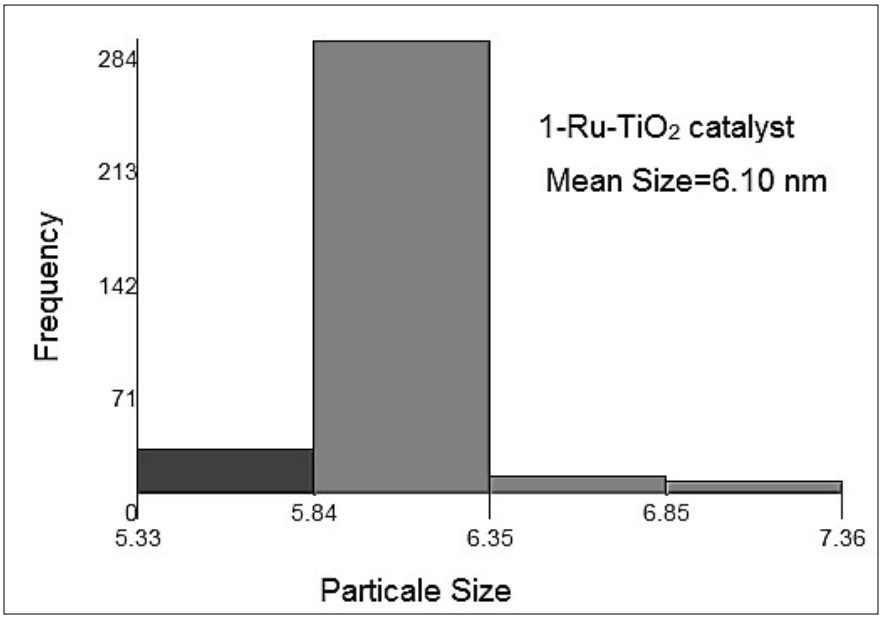
Filtration Test [1-3]

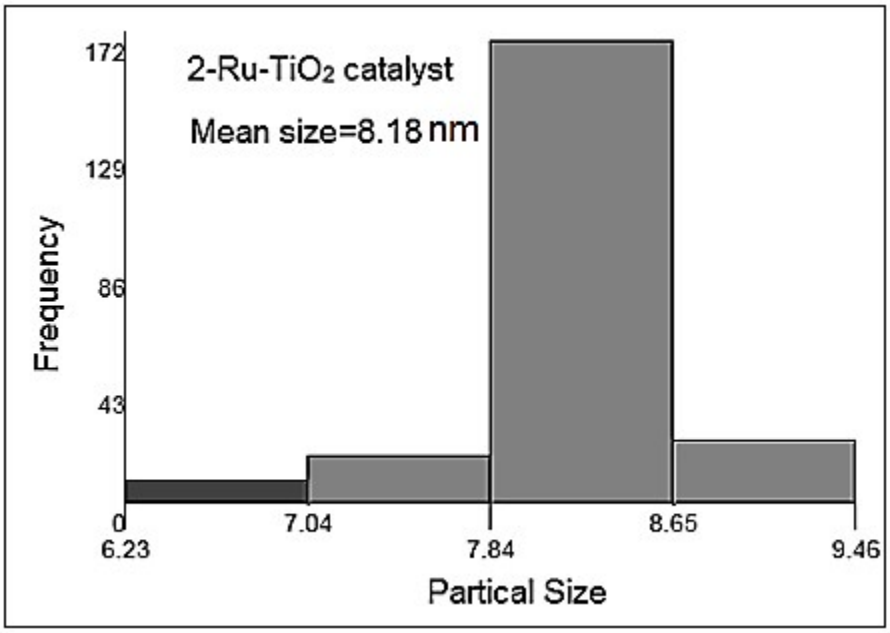
This test was performed for a comparison of the catalytic activity of 1-Ru-TiO_2 catalysts before and after filtering the active catalyst solution. In this study, the 1-Ru-TiO2 catalyst was mixed with hydrogen gas (Table 6, entry-1 reaction condition was applied). The solid was separated from the solution by using a 0.45 mm polytetrafluoroethylene (PTFE) filter and the filtrate was used for the hydrogenation reaction. No formic acid formation was confirmed negligible amount of active Ru metal catalyst leaching from the 1-Ru-TiO2 catalyst. This result was also supported by ICP-OES analysis result of filtrate where Ru metal was not detected in the solution.

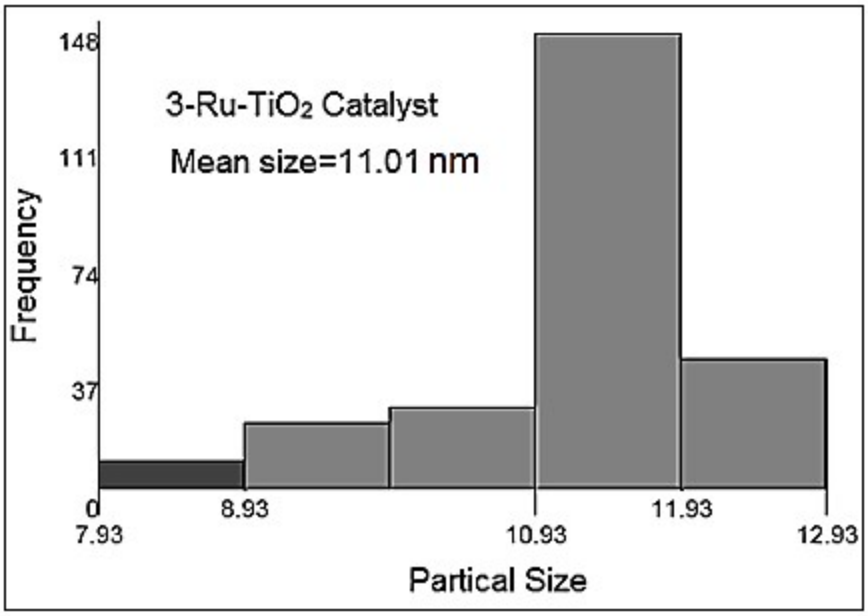
Reference:

1. A.V. Gaikwad, A. Holuigue, M.B. Thathagar, J.E. ten Elshof, G. Rothenberg, Chem. Eur. J., 2007, 6908–6913.
2. Z. Xu, N. D. McNamara, G. T. Neumann, W. F. Schneider, J. C. Hicks, ChemCatChem, 2013, 5, 1769 – 1771.
3. J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem., 2003, 198, 317–341.

Histogram Data






3-Ru-TiO2 Catalyst
Mean size=11.01 nm
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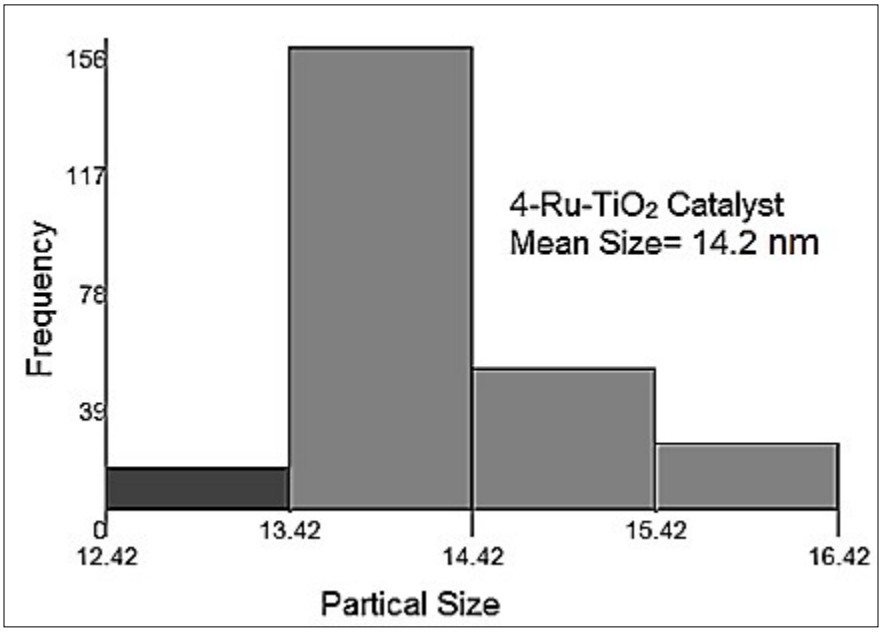
111
74
37
0
7.93
8.93
10.93
11.93
12.93
Partical Size


4-Ru-TiO2 Catalyst
Mean Size= 14.2 nm
Frequency
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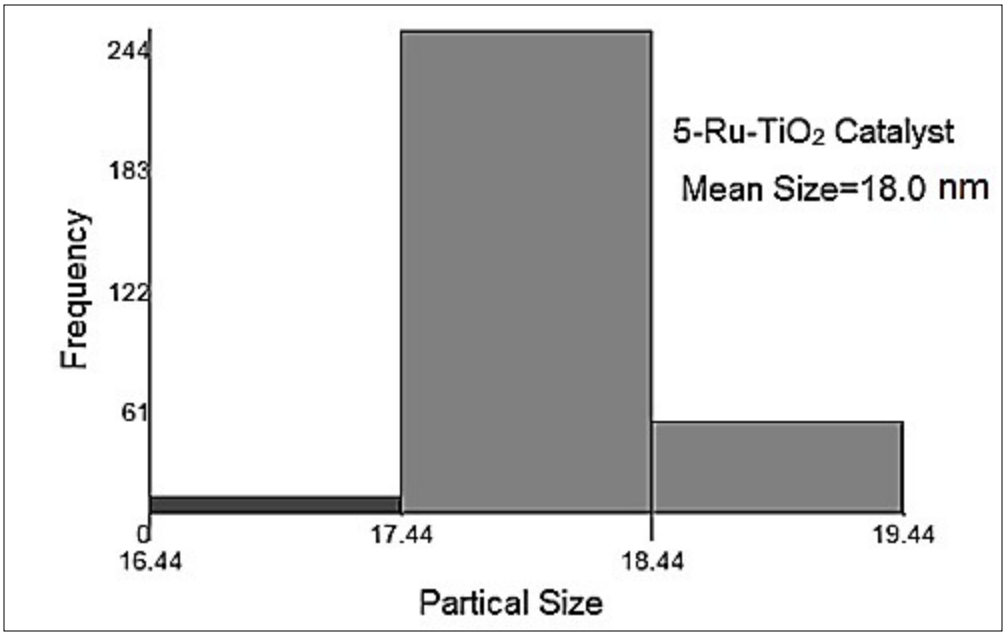
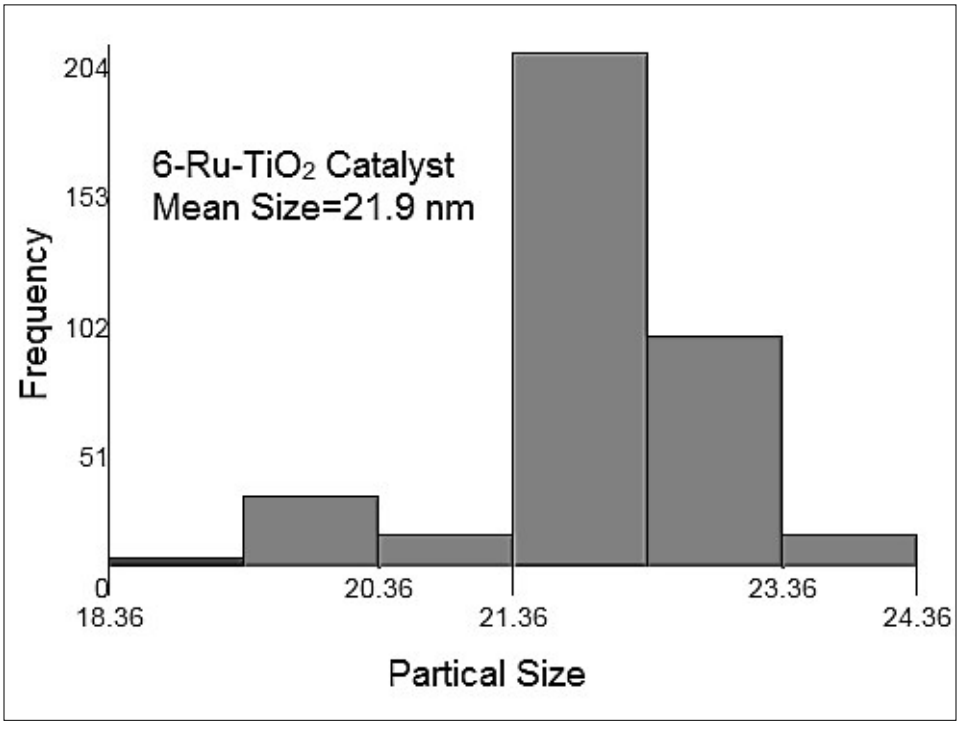
117
78
39
0
12.42
13.42
14.42
15.42
16.42
Partical Size


244
183
122
61
0
Frequency
5-Ru-TiO2 Catalyst
Mean Size=18.0 nm
16.44
17.44
18.44
19.44
Partical Size


204
153
102
51
0
Frequency
6-Ru-TiO2 Catalyst
Mean Size=21.9 nm
18.36
20.36
21.36
23.36
24.36
Partical Size