

Aqueous Phase Fischer-Tropsch Synthesis with a Ruthenium Nanocluster Catalyst

Chao-xian Xiao, Zhi-peng Cai, Tao Wang, Yuan Kou*, Ning Yan*
 PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College
 of Chemistry and Molecular Engineering, Peking University, Beijing 100871 (China)
 *yuankou@pku.edu.cn

Introduction

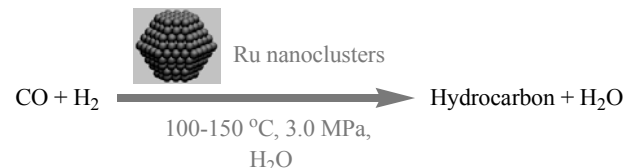
Hydrogenation of carbon monoxide to produce hydrocarbons, normally called Fischer-Tropsch synthesis (F-T synthesis),^[1] is one of the most important hydrogenation reactions due to its potential for the intermediate production of hydrocarbon fuels in the “post-petroleum” era. The reaction is favored at low-temperature and therefore reducing the particle size of the catalyst to several nanometers, while maintaining their three-dimensional freedom, may in principle significantly increase the catalytic activity as well as decrease the working temperatures for the process. It has been reported that soluble nanoclusters in ionic liquids or liquid water exhibit excellent catalytic performance in the hydrogenation of various organic substrates and also are comparatively green in nature. As far as we are aware, aqueous phase F-T synthesis has not been reported to date but it has been shown that water steam promotes the reaction (see entry 8 in Table 1).^[2] Here we report our first steps in the development of an aqueous-phase process for hydrogenation of carbon monoxide using a ruthenium nanocluster catalyst (Scheme 1).

Materials and Methods

The aqueous phase ruthenium nanocluster catalyst was prepared according to the following procedure: $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (73 mg, 2.79×10^{-4} mol of Ru) and PVP (1.240 g, 1.12×10^{-2} mol; PVP:Ru = 40:1) were dissolved in deionized water (20 ml) with stirring. The solution was placed in a 60-ml stainless steel autoclave, and then reduced under 2.0 MPa H_2 at 150 °C for 2 h with a stirring speed of 800 rpm. The resulting colloidal black solution contained ruthenium nanoclusters was used for catalytic testing.

Results and Discussion

It can be seen from Table 1 that a nanocluster ruthenium catalyst in pure liquid water has an unprecedented activity of as high as $6.9 \text{ mol}_{\text{CO}} \text{ mol}_{\text{Ru}}^{-1} \text{ h}^{-1}$ (entries 2–3) at 150 °C in the presence of 1 MPa CO and 2 MPa H_2 . This value is almost 35 times that of Ru/SiO₂ catalyst at 150 °C (entry 7) and 6–16 times that of the same catalyst at 200 °C (entry 8) in the presence of varied amounts of added steam. Indeed, even at 100 °C (entry 5) the activity of the ruthenium nanocluster catalyst in water is comparable to that of the supported Ru/SiO₂ catalyst at 200 °C (entry 8). It is noteworthy that a commercial Ru/C catalyst showed no detectable activity at 150 °C under identical reaction conditions to those employed for the nanoclusters (entry 6).



Scheme 1. Aqueous phase Fischer-Tropsch synthesis with a ruthenium nanocluster catalyst.

Table 1. Catalytic properties of Ru nanoclusters in various solvents^[a] and comparative data for conventional supported catalysts

Entry	Solvent	Reducing agent ^[b]	<i>T</i> [°C]	Activity [$\text{mol}_{\text{CO}} \text{ mol}_{\text{Ru}}^{-1} \text{ h}^{-1}$]	Aggregation after reaction
1	Water	Blank	150	0	—
2 ^[c]	Water	H_2	150	6.8	No
3	Water	H_2	150	6.9	No
4	Water	H_2	120	3.1	No
5	Water	H_2	100	0.74	No
6	5% Ru/C in 20 ml water		150	0	—
7 ^[d]	8% Ru/SiO ₂ , 0.1 MPa, $\text{H}_2/\text{CO}=1$, 500 ml/h		150	0.19	—
8 ^[e]	5% Ru/SiO ₂ , 1.5 MPa, $\text{H}_2/\text{CO}=2$, $p(\text{H}_2\text{O}) = 0.017$ -0.454 MPa.		200	0.41-1.22	—

^[a] Typical reaction conditions: 2.0 MPa H_2 , 1.0 MPa CO, 20 ml of solvent, 2.79×10^{-4} mol of Ru, PVP:Ru = 20:1. ^[b] Used for preparing the ruthenium nanocluster catalysts. ^[c] PVP:Ru = 40:1. ^[d] From literature data^[3]. ^[e] From literature data^[2].

Significance

Aqueous phase Fischer-Tropsch synthesis differs greatly from traditional Fischer-Tropsch synthesis using slurry reactors, since the catalyst is composed of nano-scale particles, which are dispersed in liquid water to form a quasi-homogenous phase system. Aqueous phase Fischer-Tropsch synthesis features in much lower reaction temperature and significantly higher activity. It also has advantages in reaction heat transferring and product separation.

References

- Fischer, F., Tropsch, H. *Brennst. Chem.* 4, 276 (1923).
- Claeys, M., van Steen, E. *Catal. Today* 71, 419 (2002).
- Turner, M. L., Marsih, N., Mann, B. E., Quyoum, R., Long, H. C., Maitlis, P. M. *J. Am. Chem. Soc.* 124, 10456 (2002).