

Efficient Nd Promoted Rh Catalysts for Vapor Phase Methanol Carbonylation

Shu Feng ZHANG, Qing Li QIAN, Ping Lai PAN, Yi CHEN*, Guo Qing YUAN*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: A Nd promoted-Rh catalysts supported on polymer-derived carbon beads for vapor-phase methanol carbonylation was developed. Rh-Nd bimetallic catalysts obviously have higher activity than that of supported Rh catalyst under similar reaction condition. The difference between the activity of above two catalyst systems is clearly caused by the intrinsic properties generated by the introduction of Nd.

Keywords: Supported catalysts, Rh-Nd bimetallic, methanol carbonylation.

The catalytic carbonylation is of great theoretical and technological importance for the development of new routes of utilization of coal. In C1 chemistry, the carbonylation of alcohol and ester are very profitable processes. Methanol carbonylation for the manufacture of acetic acid is a case in the point. The current technology is based on precious rhodium and iridium catalysts, which are dissolved in liquid phase¹⁻³. Although the processes are highly effective, the recovery and recycle of the catalyst is difficult. Further more, iodomethane and water may cause erosion of equipment parts. An efficient heterogeneous catalyst would provide great theoretical incentive to produce this valuable commodity chemical. To achieve this purpose, a Nd promoted-Rh catalyst supported on polymer-derived carbon beads⁴⁻⁵ was developed. The polymer-derived carbon beads is loaded with two active metals (rhodium and neodymium), which finely spread over the surface of the support (the grain size is not larger than 10 nm) and form Rh→C and Nd→C bonds with the surface. Based on the characterization of the novel catalyst, its properties and the superiority compared with single Rh metal have been studied by means of the carbonylation of methanol for preparing acetic acid under relative mild conditions. Experiments confirmed that addition the second kind of metal can get excellent activity and selectivity of the catalyst even when the content of rhodium was decreased.

As a support for vapor-phase methanol carbonylation⁵, the polymer-derived carbon beads showed excellent performance. The Rh and Nd were introduced by incipient wetness impregnation of the support with methanol solution of Rh-Nd (namely Rh(NO₃)₃ and NdCl₃·3H₂O). The fresh catalyst sample was reduced by hydrogen at 600°C, and further treated at 1000°C for 2 h under Ar atmosphere. The loading of Rh is 0.20%-0.25% (wt).

* E-mail: yuangq@iccas.ac.cn, chenyi@iccas.ac.cn

Via introducing the active metal with a second component, the surface metallic structure of the supported catalyst can be modified and its catalytic performance can be enhanced. **Table 1** is XPS analysis of the surface composition of bimetallic catalyst at different temperature. With the increase of treatment temperature (600°C-1000°C), the surface atomic ratio of Nd to Rh decreases from 1.319 to 1.148, and it is concluded that certain type of intermerging between two metals happens and leads to the change of their dispersion over the support surface. Another experimental observation showed that the binding energy of Nd increased with the increase of treatment temperature. It indicates that Nd has modified the metallic structure of Rh (supported Rh particles).

Heterogeneous catalysis is a surface phenomenon. The surface area of active centres is an important parameter affecting the catalyst activity. The second component also influences the dispersion of supported Rh particles and changes the surface area of Rh particles. Generally, high treatment temperature increases the propensity to sinter and causes conglomeration⁶. But our experimental observation demonstrates that elevation of thermal treatment temperature has led to the high dispersion of supported metal particles (**Figure 1**). **Figure 1a** is the TEM at 600°C and **Figure 1b** is the TEM at 1000°C respectively. The TEM showed that elevation of the treatment temperature led to improve the dispersion of Rh particles. **Figure 1a** shows Rh particle size is about 40-100 nm and it is 14-4 nm in **Figure 1b**. It is clear that the introduction of Nd affects metal particle growth and redispersion of supported Rh.

The introduction of Nd can influence the adsorption process of methanol and the surface reaction over the catalyst particles, in addition, it changes the catalytic activity and selectivity of the catalyst. Our experiment results for the catalyst demonstrate that the influence is positive.

Figure 1 TEM images of Rh, Nd catalyst at 600°C and 1000°C

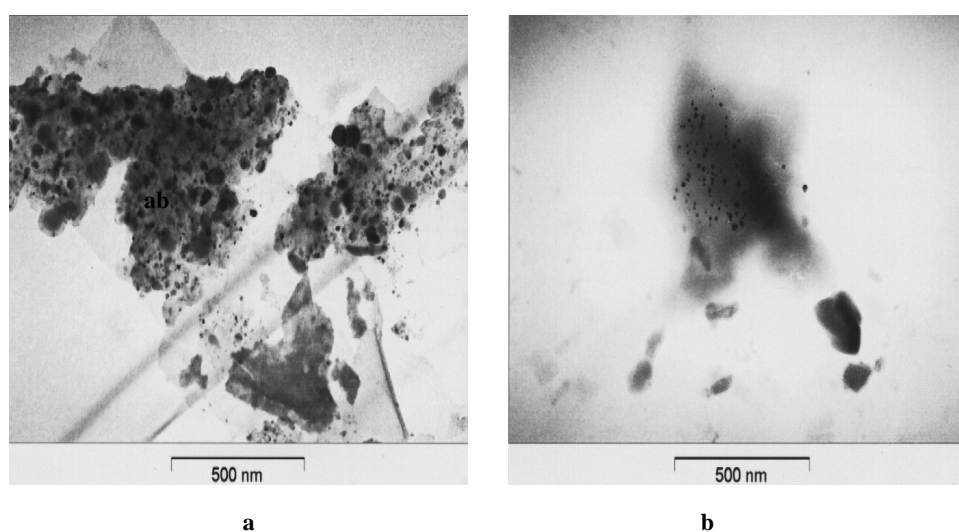


Table 1 XPS analysis of the surface composition of bimetallic catalyst at different temperature

T	Elements	Binding Energy (ev)	[AT]%	$[AT]_{Nd}/[AT]_{Rh}$
600 °C	Nd3d	982.15	0.918	1.319
	Rh3d	309.00	0.696	
1000 °C	Nd3d	982.75	0.581	1.148
	Rh3d	306.90	0.506	

Table 2 Catalytic comparison between Rh-Nd/ and Rh catalyst

Catalysts	Content of Rh (%)	Content of Nd (%)	Catalytic rate (g AcOH/g Rh·h)
Rh	0.20	0.00	120
Rh-Nd ^{1#}	0.20	0.20	160
Rh-Nd ^{2#}	0.25	0.25	190

Reaction condition: temperature 200 °C, pressure 1.0MPa,
CH₃OH/CH₃I = 4:1(V/V), flow of liquid 0.3 mL/min

The measurement of catalytic activity of the catalysts was carried out in a fixed-bed reactor (FBR). The feed gas, composed of methanol, carbon monoxide and iodomethane, was passed through the catalyst bed. The gas chromatograph (GC 8180) was used to analyze the feed gas and the outlet product. The reaction temperature and total pressure were controlled. The results of measurement are presented in **Table 2**. The catalytic activity of supported Rh-Nd bimetallic catalysts is obviously higher than that of supported Rh catalyst under similar reaction conditions. The difference between catalytic activity of the catalysts, as shown in **Table 2**, is due to the intrinsic properties generated by introduction of Nd.

References

1. M. K. Guerra, Acetic Acid and Acetic Anhydride, SRI International, Mento Park, CA, **1994**, Report No. 37B.
2. Y. Noriyuki, K. Satoru, Y. Makoto, P. Peter, W. Steve, *Appl. Catal. A*, **2001**, 221, 253.
3. G. J. Sunley, D. J. Waston, *Catal. Today*, **2000**, 58, 293.
4. F. B. Li, J. Huang, J. Zou, P. I. Pan, G. Q. Yuan, *Carbon*, **2002**, 40, 2871.
5. F. B. Li, J. Huang, J. Zou, P. I. Pan, G. Q. Yuan, *Appl. Catal. A*, **2003**, 295, 251.
6. C. H. Bartholomew, *Appl. Catal. A*, **2001**, 17, 212.

Received 17 December, 2003