

Fabrication of zeolite-4A membranes on a catalyst particle level

Yijun Zhong,^{*a} Liang Chen,^{ab} Mengfei Luo,^a Yunlong Xie^a and Weidong Zhu^c

Received (in Cambridge, UK) 1st March 2006, Accepted 24th April 2006

First published as an Advance Article on the web 5th June 2006

DOI: 10.1039/b603128e

Zeolite-4A membranes are coated onto spherical Pt/ γ -Al₂O₃ particles with an average diameter of 1.5 mm, and a model oxidation reaction of a mixture of CO and *n*-butane (50 : 50) is used to demonstrate the concept of reactant selectivity *via* the coated defect-free membranes.

The concept of reaction selectivity enhanced *via* molecular sieve membranes coated onto catalyst particles was originally proposed by Foley *et al.*,¹ who anticipated the selective formation of dimethylamine over a catalyst particle coated with a carbon molecular sieve layer. Since then, only a few researchers have utilized the concept to develop zeolite-coated composite catalysts for particular purposes. For example, Van der Puil *et al.*^{2,3} used silicalite-1/Pt/TiO₂ slabs and silicalite-1/Al₂O₃ composite catalysts for selective hydrogenation and alkylation, respectively. Nishiyama *et al.*⁴⁻⁶ coated silicalite-1 membranes onto silica/alumina and Pt/TiO₂ particles for the selective formation of *para*-xylene in the disproportionation of toluene, and for the selective hydrogenation of a mixture of linear 1-hexene and dibranched 3,3-dimethylbut-1-ene, respectively. Although the enhancement of high reactant and/or product selectivity through coated silicalite-1 membranes, based on a difference in diffusivity between reactants and/or products, has been achieved, the application has been limited to relatively large reactant and/or product molecules, and no absolute selectivity has been observed.

The application of zeolite-4A membranes has so far focused mainly on pervaporation for dehydration. Only limited work has been conducted on gas separation by zeolite-4A membranes.⁷⁻¹⁰ In view of their window opening sizes, zeolite-4A membranes may be applicable in the separation of some small molecules, such as H₂, CO, O₂, *etc.*, from large molecules, such as hydrocarbons, and a molecular sieving effect can be expected.

Here we report a novel strategy for the synthesis of defect-free zeolite-4A membranes on Pt/ γ -Al₂O₃ particles. A model oxidation reaction of a mixture of CO and *n*-butane was chosen to evaluate the quality of the formed zeolite membranes on the catalyst particles, and yet also demonstrate the concept of reactant selectivity *via* the coated membranes.

The spherical γ -Al₂O₃ particles, with an average diameter of 1.5 mm (BET surface area of 88 m² g⁻¹), as shown in Fig. 1(a), were calcined at 1273 K for 4 h, before the preparation of 0.5 wt% Pt/ γ -Al₂O₃ catalyst by a wet impregnation method using

H₂PtCl₆·6H₂O as the precursor. The as-synthesized catalyst was calcined at 773 K for 6 h prior either to zeolite-4A membrane coating or oxidation reaction testing.

The mixture used for zeolite-4A membrane coating had a molar composition of 2.25SiO₂·16Na₂O·1Al₂O₃·445H₂O. The aluminium source was NaAlO₂ and the silicon source was Na₂SiO₃. Either the aluminium or silicon source solution was filtered through a 0.22 μ m filter. The two source solutions were then mixed with vigorous stirring for 15 min. The reaction mixture was aged for 1 h at room temperature before being added into a polyethylene bottle with a layer of the Pt/ γ -Al₂O₃ particles pretreated in the following way: immersed in a 5% NaOH solution for 15 min, washed with de-ionized water and subsequently dried at 393 K for 1 h. The zeolite coatings onto the Pt/ γ -Al₂O₃ particles were performed in an oven at 353 K for a typical period of 3 h. Afterwards, the polyethylene bottle was removed from the oven and cooled to room temperature. The particles were recovered then washed with de-ionized water and subsequently dried at 373 K overnight. This zeolite-4A composite catalyst, made by the one-step synthesis, is referred to as NaA(1)/Pt/ γ -Al₂O₃. Fig. 1(c) shows a typical SEM image of this zeolite-coated particle from a top

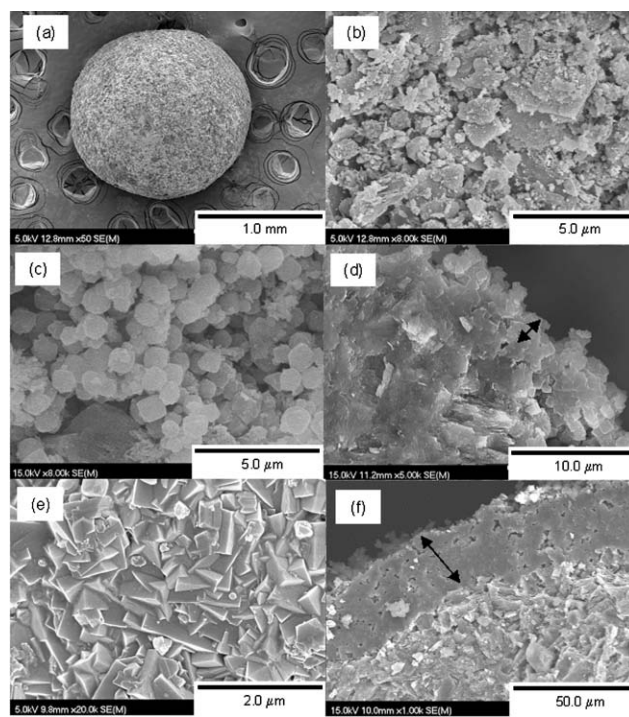


Fig. 1 SEM images of (a) and (b): Pt/ γ -Al₂O₃, (c) and (d): NaA(1)/Pt/ γ -Al₂O₃, and (e) and (f): NaA(2)/Pt/ γ -Al₂O₃. (a), (c) and (e) are top views. (b), (d) and (f) are cross-section views.

^aZhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, Zhejiang, China. E-mail: yjzhong@zjnu.cn; Fax: +86-579-2282595; Tel: +86-579-2282543

^bDepartment of Chemistry, Zhejiang University, Hangzhou 310027, China

^cReactor and Catalysis Engineering, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

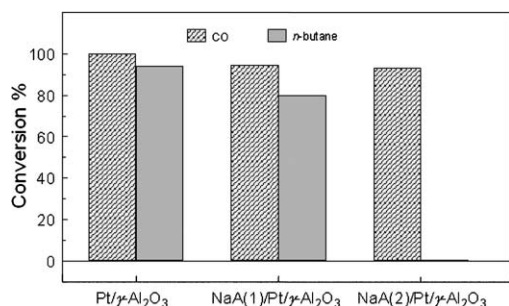


Fig. 2 Component conversions of CO and *n*-butane from equimolar mixtures during oxidation over Pt/ γ -Al₂O₃, NaA(1)/Pt/ γ -Al₂O₃ and NaA(2)/Pt/ γ -Al₂O₃ at 483 K after 1 h of reaction (steady state).

view, indicating that the surface of the Pt/ γ -Al₂O₃ particle is loosely covered with small zeolite-4A crystals. From the cross-section view in Fig. 1(d), a very thin zeolite layer was formed on the particle.

Following the same procedure described above, NaA(1)/Pt/ γ -Al₂O₃ particles were also used as a support for the zeolite coatings; the so-called two-step synthesis, in which a slightly different synthesis mixture molar composition of 2.25SiO₂·10Na₂O·1Al₂O₃·445H₂O was used. The synthesized composite catalyst prepared in this manner is referred to as NaA(2)/Pt/ γ -Al₂O₃. As shown in Fig. 1(e), the particle surface is densely covered with inter-grown cubic zeolite-4A crystals. Its visual thickness was about 20 μ m, indicated from the cross-section view in Fig. 1(f), much thicker than the coating by the one-step synthesis.

The oxidation reactions of CO and *n*-butane mixtures over Pt/ γ -Al₂O₃, and over the synthesized composite catalysts NaA(1)/Pt/ γ -Al₂O₃ and NaA(2)/Pt/ γ -Al₂O₃, were carried out using a fixed-bed reactor (pyrex tube with an inner diameter of 6 mm) under continuous flow and atmospheric pressure conditions. In all cases, the amount of loaded catalyst was 1 g, and the feed flow rates of air, CO and *n*-butane were 96, 2 and 2 ml (normal temperature and pressure, NTP) min⁻¹ (NTP: 298 K and 101.3 kPa), respectively. The reactor, inserted in an oven, was heated at a ramp rate of 1 K min⁻¹ to the desired temperature. The concentrations of CO and *n*-butane in the outlet of the reactor were determined by an infrared CO gas analyzer and a GC equipped with an FID, respectively.

The kinetic diameters of CO (0.37 nm) and O₂ (0.35 nm) are smaller than the 8-membered ring window opening size of zeolite-4A (0.4 nm), while the latter is larger than the kinetic diameter of *n*-butane molecules (0.43 nm). A molecular sieving effect can therefore be expected for a well inter-grown zeolite-4A membrane, and inherently an absolute selectivity for CO oxidation in its mixture with *n*-butane should be observed.

Fig. 2 summarizes the component conversions of CO and *n*-butane in an equimolar mixture during oxidation over the three different catalysts at 483 K. Under the applied conditions, the CO is completely oxidized and the conversion of *n*-butane is about 95% over Pt/ γ -Al₂O₃, indicating that the selectivity for CO over *n*-butane is very minor. Similarly, over NaA(1)/Pt/ γ -Al₂O₃ catalyst, there is no significant selectivity for CO, but both oxidation conversions are slightly lower. As indicated in the SEM images in Fig. 1(c) and (d), after the one-step synthesis, the formed zeolite

layer on the Pt/ γ -Al₂O₃ particle contains non-zeolitic interstitial pores. Consequently, both CO and *n*-butane can easily pass through these pores, resulting in no significant oxidation selectivity for CO over *n*-butane.

It is interesting to note that the oxidation conversion of the *n*-butane over NaA(2)/Pt/ γ -Al₂O₃ is practically zero, which is not clearly indicated in Fig. 2. This is fully attributable to the molecular sieve effect, *i.e.* the reactant *n*-butane cannot pass through the densely formed zeolite layer on Pt/ γ -Al₂O₃ to reach to the catalytic species. On the other hand, the reactants CO and O₂ can diffuse through the zeolite-4A interstitial pores, and this oxidation takes place on Pt/ γ -Al₂O₃. The result in Fig. 2 shows that the conversion of CO is maintained as high as 93%, although it is slightly lower than that over the catalyst without any zeolite-4A coatings, probably due to some diffusion limitation of the reactants CO and O₂, as well as the product CO₂, through the thicker but defect-free membrane layer.

In general, zeolite membranes may contain certain pinholes. Consequently, the separation performance of zeolite membranes depends significantly on the membrane quality, because defects existing among the crystals can reduce selectivity dramatically. The most common method of suppressing these defects in zeolite-4A membranes is to grow a thicker zeolite layer, where each new layer of crystals covers the defects in the previous layer. This has been confirmed by the current approach.

In conclusion, defect-free zeolite-4A membranes have been successfully coated onto Pt/ γ -Al₂O₃ particles, carried out by a two-step synthesis. A model oxidation reaction of a mixture of CO and *n*-butane over this composite catalyst has demonstrated the concept of reactant selectivity *via* coated defect-free membranes. Since a trace amount of CO often co-exists in hydrocarbon feed streams and CO can poison the catalysts of desirable reactions, the removal of the CO from these feed streams can become very necessary. Therefore, the current study shows that the selective oxidation of CO over zeolite-4A-coated catalyst particles might provide a suitable method.

The financial support provided by the National Science Foundation of China (code 20471052) is gratefully acknowledged.

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