JOURNAL OF CATALYSIS **180,** 51–55 (1998)
ARTICLE NO. CA982261

Glucose Hydrogenation on Ruthenium Catalysts in a Trickle-Bed Reactor

Pierre Gallezot,*,[1] Nathalie Nicolaus,* Guy Flèche,† Patrick Fuertes,† and Alain Perrard*

*Institut de Recherches sur la Catalyse-CNRS, 2, Avenue Albert Einstein, 69626 Villeurbanne Cédex, France;
and †Société Roquette Frères, 62136 Lestrem, France

Received April 21, 1998; revised August 14, 1998; accepted August 18, 1998

Glucose in 40 wt% aqueous solution was hydrogenated into sorbitol in a trickle-bed reactor over ruthenium catalysts supported on active charcoal pellets. The metal was loaded by cationic exchange or anionic adsorption. After reduction, ruthenium was under the form of 1-nm particles homogeneously distributed throughout the support. The reaction was conducted at 100°C under 8 MPa of hydrogen at 20 L h^{-1} flow rate. Conversion and selectivity to sorbitol were studied as a function of residence time. Whatever the mode of preparation, the catalysts give a total conversion of glucose with an initial specific activity of 1.1 mol h^{-1} g_{Ru}^{-1}. The selectivity to sorbitol was higher than 99.2% at 100% conversion; however, the liquid flow rate should be adjusted very accurately because any increase in the residence time results in a loss of selectivity due to epimerization of sorbitol into mannitol. The catalyst activity was stable over several weeks and no leaching of ruthenium was detected.

INTRODUCTION

Sorbitol is a major specialty product prepared by catalytic hydrogenation of glucose, which is a cheap and abundant feedstock obtained from renewable resources, particularly from starch-containing crops such as maize and wheat. Sorbitol is used as an additive in many industrial products, particularly in the food, cosmetic, and paper industries, and as a building block in the synthesis of various fine chemicals, including vitamin C. Most of the industrial production is based on the hydrogenation of glucose in a batch process employing nickel-based catalysts in powder form, particularly Raney nickel promoted by various transition metals. In a previous study (1), the effects of molybdenum, chromium, iron, and tin promoters on activities and selectivities of Raney nickel were studied. There are currently strong incentives to develop continuous hydrogenation processes to cope with the increasingly larger demand for sorbitol (ca. 700,000 tons/year). The challenge is to obtain a selectivity to sorbitol higher than 99% at 100% conversion and a high stability of the catalyst during a long period of time. To meet the stability challenge, the catalyst should be resistant to metal sintering and poisoning, but the most crucial point is to avoid metal and support leaching in the acidic and chelating reaction medium. In a previous work, the kinetics of glucose hydrogenation was studied in a trickle-bed reactor in the presence of kieselguhr-supported nickel catalysts (2). It was shown that glucose was converted to sorbitol according to a Langmuir–Hinshelwood rate law where the reaction between adsorbed glucose and dissociated hydrogen was rate-determining. However, the activities decreased with time because of the progressive leaching of both nickel and support. Ruthenium, which is much more active than nickel in the hydrogenation of aqueous solutions of glucose (3), is potentially a good substitute for nickel in fixed-bed catalytic processes. Makkee *et al.* (4) studied the hydrogenation of glucose and glucose–fructose mixtures in ruthenium catalysts, but their primary aim was to obtain the highest mannitol yield, which was better achieved with Cu/SiO_2 catalyst combined with enzymatic isomerization. Two studies of glucose hydrogenation in a trickle-bed reactor were conducted by Germain *et al.* (5) and Arena (6). The former authors established a rate law but did not give precise data on selectivities. Arena did not give data on activities and selectivities, but showed that Ru/Al_2O_3 catalysts deactivated because of the presence of iron and sulfur impurities and because the physical properties of the alumina support were modified. In the present work, glucose hydrogenation was conducted in a trickle-bed reactor in the presence of carbon-supported ruthenium catalysts. Ruthenium and carbon were chosen because both metal and support are stable in the reaction medium under hydrogenation conditions. The activities, selectivities, and stabilities of ruthenium catalysts prepared by anionic adsorption or cationic exchange were compared.

EXPERIMENTAL

Preparation of Catalysts

Extrudates of activated carbon Norit rox 0.8 were employed because of their high purity, suitable resistance to attrition, and small size (cylinders of 0.8-mm diameter),

---

[1] To whom correspondence should be addressed. E-mail: gallezot@catalyse.univ-lyon1.fr.

0021-9517/98 $25.00

which should minimize internal diffusion limitation. The support was used as such for metal loading by anionic adsorption, but was oxidized to create acidic functional groups for preparation by cationic exchange. Chemical oxidation was achieved by treating 20 g of active carbon with an aqueous solution of sodium hypochlorite (380 mL, 5% active chlorine) at room temperature. The solution was added slowly to the suspension, which was stirred at 120 rpm for 20 h. The active carbon was then washed with hydrochloric solutions (1 mol L^{-1}) to eliminate sodium ions and then with water until the wash-waters were chlorine free.

Catalyst 1.6% Ru/C_{ex} was prepared by cationic exchange and hydrogen reduction. The oxidized support was stirred in ammonia solution (200 mL, 1 mol L^{-1}) in the presence of bubbling nitrogen. Required amounts of $Ru(NH_3)_6Cl_3$ in molar ammonia solution were then added to the suspension, which was stirred for 24 h at room temperature and then filtered. The solid was washed until neutrality of the wash waters was reached and dried at 100°C for 15 h in nitrogen atmosphere. Catalyst 1.6% Ru/C_{ex} was reduced by heating under flowing hydrogen at 2°C min^{-1} from 25 to 227°C, maintained at this temperature for 3.5 h, cooled under nitrogen, and then contacted with a mixture of 1% O_2 in N_2 flowing at 6 L h^{-1} for 3 h.

Catalysts 1.8% Ru/C and 1.7% Ru/C were prepared by anionic adsorption and liquid-phase reduction. The support (29.4 g) was suspended in 300 mL of demineralized water in the presence of bubbling nitrogen. A total of 48.2 mL of $RuCl_3$, H_2O in a molar hydrochloric acid solution (12.44 g_{Ru} L^{-1}) was added to the suspension, which was stirred for 5 h. The suspension maintained under nitrogen atmosphere was cooled to 0°C. Then 75 mL of a formaldehyde solution (37%) and 40 mL of a potassium hydroxide solution (30%) were added to the suspension under continuous stirring. After 15 h, the suspension was filtered, and the solid was washed with water until neutrality of wash waters and then dried under flowing nitrogen at 100°C.

Reaction Procedure

Experiments were carried out in a micropilot trickle-bed reactor LCT 570 from Vinci Technologies described previously (2). Hydrogen from a gas cylinder was depressurized to 2–20 MPa and its flow rate was set by a mass flow controller (Brook 5850TR) giving a constant flow of 10 to 100 L h^{-1}. Degassed aqueous solutions of glucose were injected with a high-pressure pump (30–800 mL h^{-1}). Hydrogen and glucose solution flows were mixed at the inlet of the reactor, which consisted of a stainless steel tube (length, 330 mm; internal diameter, 15.8 mm; internal volume, 60 cm^3). Gas and liquid were flown in co-current downflow mode through the reactor containing the catalyst bed placed between two layers of glass beads. The catalyst bed was in the isothermal zone of the reactor obtained by differential heating along the oven; the temperature was controlled by a thermocouple immersed in the catalyst bed. At the reactor outlet, the liquid and gas flows were cooled and recovered in the gas–liquid separator. The gas flow was depressurized to atmospheric pressure by a back-pressure regulator (Brook 5835P). The liquid was continuously withdrawn with an automatic valve regulated by a manometer measuring the differential pressure in the gas–liquid separator.

The product distribution was measured by analysis of liquid samples taken from the gas–liquid separator at various time intervals. Analyses were performed by HPLC after separation on an Aminex HPX-87C column from Bio-Rad maintained at 85°C. From time to time products were also analyzed by GC using α-methyl-D-glucopyranoside as internal standard after silylation of the molecules in pyridine with hexamethyldisilazane and trimethylchlorosilane. Residual glucose concentration after reaction was also measured by Bertrand's method.

Hydrogenation of glucose solutions (40 wt% or 2.6 mol L^{-1}) was carried out continuously for long periods (typically 2 to 5 weeks) under standard reaction conditions (100°C; H_2 pressure, 8 MPa; H_2 flow rate, 20 L h^{-1}; glucose solution flow rate, 36 mL h^{-1}) on a given catalyst. The liquid flow rate was changed from time to time to study the effect of residence time on activity and selectivity; the residence time was defined as the ratio of the mass of ruthenium/liquid flow rate, and thus expressed in g_{Ru} h mL^{-1}. The initial specific activities were obtained by measuring the slope, at short residence time, of the curve giving the conversion vs residence time. The mean specific activities corresponding to a given conversion were also obtained from the conversion vs residence time curve.

Characterization of Catalysts

The ruthenium content of catalysts was determined by ICP-AES after dissolution of the solid in acidic and oxidizing medium. The size and distribution of metal particles in the carbon support were determined on ultramicrotome thin sections of the catalysts by high-resolution transmission electron microscopy (TEM) with a JEOL 100 CX microscope.

RESULTS AND DISCUSSION

Catalyst Prepared by Cationic Exchange

The TEM views of ultramicrotome sections of catalyst 1.6% Ru/C_{ex} showed that the size of ruthenium particles was about 1 nm or less. The particles were very homogeneously distributed in the support. This is in agreement with previous works (7, 8) showing that in Ru/C catalysts prepared by the same exchange method, most of the particles were smaller than 1 nm and homogeneously distributed throughout the support.

TABLE 1

Catalytic Data Measured after Varying Time on Stream During Continuous Hydrogenation of Glucose Solution on 1.6% Ru/C_{ex}

Entry	Time on stream (h)	Conversion[a] (%)	Selectivity[a] (%)		Mean activity[b] (mmol h^{-1} g_{Ru}^{-1})
			Sorbitol	Mannitol	
1	29	98.0	99.4	0.6	696
2	45–52[c]	98.5	99.6	0.4	700
3	52–69[c]	98.6	99.5	0.5	700
4	312	94.4	99.4	0.6	670

[a] From HPLC measurements.

[b] Mean activity for the given conversion.

[c] Liquid sample collected during specified time interval. Reaction conditions, 40 wt% glucose aqueous solution; flow rate, 36 mL h^{-1}; hydrogen pressure, 8 MPa; H_2 flow rate, 100 L h^{-1}; temperature, 100°C; catalyst, 1.6% Ru/C_{ex}; catalyst mass, 8.25 g.

Glucose hydrogenation on 8.25 g of the 1.6% Ru/C_{ex} catalyst was conducted continuously at 100°C under 8 MPa of H_2 pressure for 363 h. As the hydrogen flow rate was 20 mL h^{-1}, the catalyst deactivated, but the activity was regenerated by running the reaction at 100 mL h^{-1}; therefore, subsequent measurements were carried out at the latter flow rate. Table 1 gives the reaction data measured at various time intervals as the reaction was conducted at a constant residence time of 36.7 10^{-4} g_{Ru} h mL^{-1} (i.e., 36 mL h^{-1} liquid flow rate). Glucose conversion and selectivity to sorbitol were obtained from HPLC measurements, but a check of the hydrogenated solutions collected between 45 and 69 h revealed that the glucose conversion (98.8%) was very close to that measured by GC analysis (98.6%). A complete glucose conversion could not be achieved because the reactor was not loaded with enough catalyst and the residence time could not be increased because the liquid pump could not reliably deliver lower liquid flow rates. Table 1 shows that the mean activity and conversion decreased after a long time on stream. Part of the deactivation could be due to ruthenium particle sintering since a moderate particle growth was detected with another catalyst (vide infra). Poisoning of the ruthenium by metal impurities as observed earlier by Arena (6) could also well occur. However, since it was noticed that the activity decreased more rapidly at low hydrogen flow rates, the deactivation could be due to a decrease in the hydrogen coverage of ruthenium particles.

The selectivity to sorbitol measured by HPLC was very high and close to 99.5% during the entire reaction run (Table 1). However, it was slightly overestimated in comparison with that determined by GC measurements (99.1%), because the latter analysis technique allowed us to detect by-products such as iditol (0.2%) and arabitol or galactitol (0.2%).

The reaction was also studied at higher flow rates to obtain catalytic data at lower values of residence time. Figure 1 gives the glucose conversion as a function of residence time. The specific activity at low conversion (or initial specific activity) calculated from the slope of the curve was 1080 ± 50 mmol h^{-1} g_{Ru}^{-1}. The corresponding turnover frequency, calculated with a dispersion of ruthenium close to 100% as indicated by the TEM results, was 110 h^{-1}. The selectivity to sorbitol was 100% because the isomerization of sorbitol into mannitol was negligible at short contact times. The activity of our catalyst was higher than that deduced from the rate law established by Germain *et al.* (5). Indeed, under the same reaction conditions, the specific rate of glucose hydrogenation calculated from their rate law was 210 mmol h^{-1} g_{Ru}^{-1} compared to 1080 mmol h^{-1} g_{Ru}^{-1} measured on 1.6% Ru/C_{ex}.

Catalysts Prepared by Anionic Adsorption

TEM of an ultramicrotome section of the fresh 1.8% Ru/C catalyst prepared by anionic adsorption showed that the ruthenium particles were smaller than 1 nm. However, after 693 h on stream, some sintering occurred. TEM after reaction showed that some Ru particles were still smaller than 1 nm, but others were in the size range of 1 to 2 nm. Analysis by ICP-AES of the hydrogenated solutions and of the catalyst after reaction showed no loss of ruthenium.

Table 2 gives the rate and selectivity data measured on 15.25 g of 1.8% Ru/C catalyst at high residence times (76.3 10^{-4} and 68.6 10^{-4} g_{Ru} h mL^{-1} corresponding to entries 1–4 and 5, respectively). The residence time was too high since a 100% conversion was measured during the whole period of 25 days on stream. Therefore, the mean activities measured at 100% conversion and fixed residence time were constant (342 mmol h^{-1} g_{Ru}^{-1} at 76.3 10^{-4} g_{Ru} h mL^{-1}). This might mask a possible catalyst deactivation; however, measurements conducted at slightly higher residence times indicated that the deactivation, if any, should be very small. Indeed, Fig. 2 shows that the conversion decreased below 100% for residence times smaller than ca. 65 10^{-4} g_{Ru} h mL^{-1}. Since the reaction was run with a residence time of

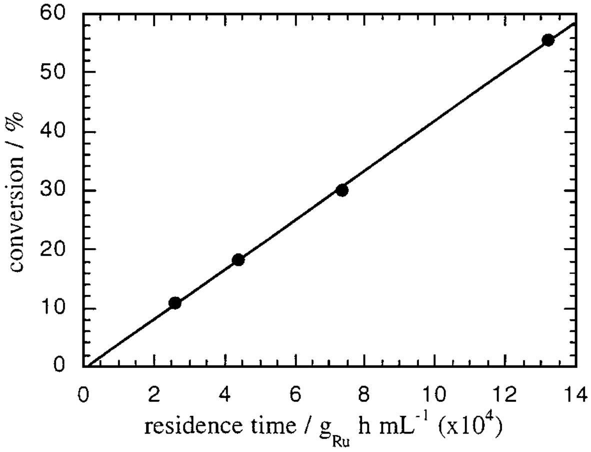

FIG. 1. Glucose conversion at short residence times on 1.6% Ru/C_{ex}.

TABLE 2

Catalytic Data Measured after Varying Time on Stream During Continuous Hydrogenation of 40 wt% Glucose Solution on 1.8% Ru/C

Entry	Time on stream (h)	Conversion (%)	Selectivity[a] (%)		Mean activity[b] (mmol h^{-1} g_{Ru}^{-1})
			Sorbitol	Mannitol	
1	39[c]	100.0	98.5	1.5	342
2	87[c]	100.0	98.4	1.6	342
3	230[c]	100.0	98.8	1.2	342
4	500[c]	100.0	99.1	0.9	342
5	596[d]	100.0	99.3	0.7	380

[a] From HPLC measurements.

[b] Activity for the given conversion.

[c] Flow rate, 36 mL h^{-1}.

[d] Flow rate, 40 mL h^{-1}. Reaction conditions, hydrogen pressure, 8 MPa; H_2 flow rate, 100 L h^{-1}; temperature, 100°C; catalyst, 1.8% Ru/C; catalyst mass, 15.25 g.

68.6 10^{-4} g_{Ru} h mL^{-1}, i.e., just above this limit, even a small deactivation would have been detected during 25 days on stream. The reaction rate at low conversion (initial rate) was very similar to that found for the 1.6% Ru/C_{ex} catalyst (1100 ± 50 mmol h^{-1} g_{Ru}^{-1}).

The selectivity to sorbitol measured at residence times lower than 50 10^{-4} g_{Ru} h mL^{-1} was higher than 99.5%, but decreased at higher contact time (Fig. 2). The influence of high residence times on the selectivity was studied by using as feedstock the solutions containing more than 99% sorbitol obtained in a first reaction run with a residence time of 68.6 10^{-4} g_{Ru} h mL^{-1}. Figure 2 shows that the selectivity to sorbitol decreased just before the 100% conversion was attained. Simultaneously mannitol formation increased, indicating that sorbitol was isomerized into mannitol. Therefore, the highest sorbitol yields can be obtained by conducting the reaction at a residence time as close as possible to that giving 100% glucose conversion, higher contact times being detrimental to sorbitol yield.

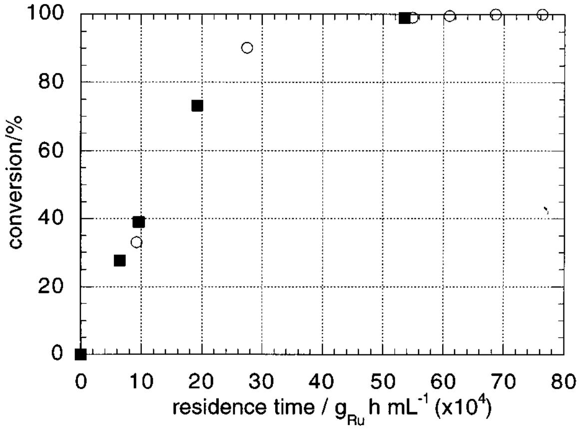

FIG. 3. Glucose conversion as a function of residence time: 10.7 g of 1.8% Ru/C catalyst (■); 15.25 g of 1.8% Ru/C catalyst (○).

The effect of catalyst mass was studied by comparing experiments conducted with 10.7 and 15.25 g of 1.8% Ru/C catalysts. Figure 3 shows that similar conversion vs residence time curves were obtained. The fact that specific rates were independent of the catalyst mass may indicate that the reaction kinetics was not perturbed by external diffusion limitation.

Another catalyst, 1.7% Ru/C, was prepared by anionic adsorption in the same way as 1.8% Ru/C. Glucose hydrogenation was studied on 16.1 g of this catalyst under the same reaction conditions as those used for 15.25 g of 1.8% Ru/C. The comparison of the two catalysts is given in Fig. 4. The data points giving the conversion as a function of residence time are very similar for the two catalysts. This suggests that the preparation of catalysts and their properties are quite reproducible.

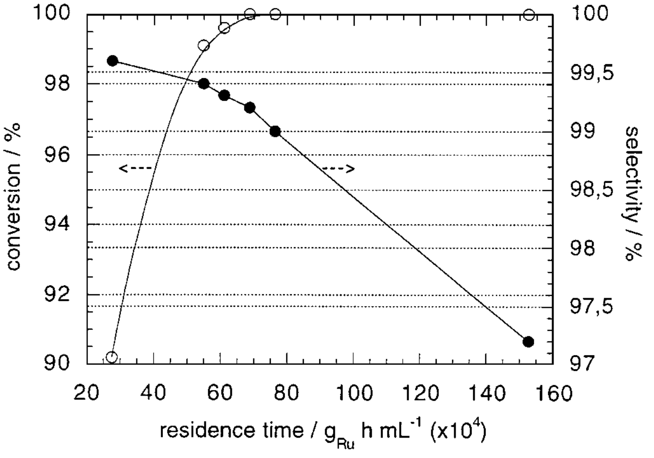

FIG. 2. Glucose conversion (○) and selectivity to sorbitol (●) measured at high residence times on 1.8% Ru/C catalyst (15.25 g).

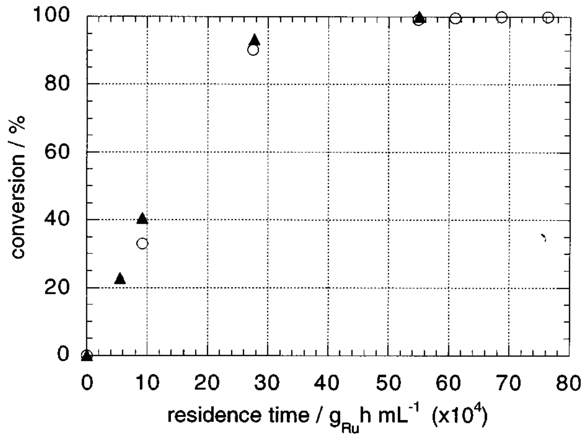

FIG. 4. Glucose conversion vs residence time on 16.1 g of 1.7% Ru/C catalyst (▲) and 15.25 g of 1.8% Ru/C catalyst (○).

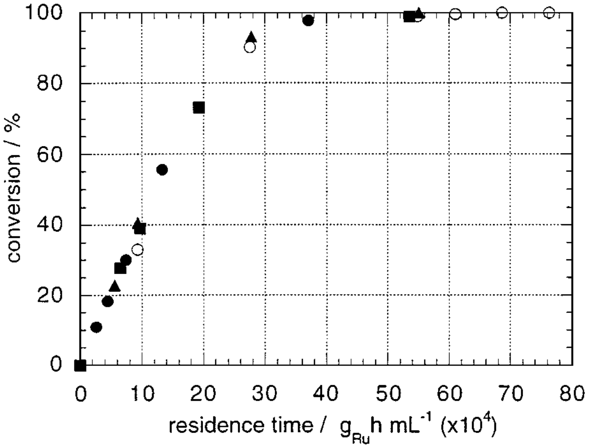

FIG. 5. Conversion of glucose vs residence time, comparison of four experiments; 8.25 g of 1.6% Ru/C_{ex} catalyst (●); 15.25 g of 1.8% Ru/C catalyst (○); 10.7 g of 1.8% Ru/C catalyst (■); 16.1 g of 1.7% Ru/C catalyst (▲).

Comparison of Catalysts

Figure 5 gives the conversion vs residence time data points for all ruthenium catalysts investigated. These points are remarkably well aligned, showing that the specific activities are similar for all catalysts. This is not surprising since the dispersion and distribution of the ruthenium particles were very similar in all catalysts prepared by either cationic exchange or anionic adsorption on the same catalyst support. Modeling the reaction kinetics was not attempted because, given the high reaction rates, the data could be perturbed by mass transfer limitation, which would affect all catalysts to the same extent because of their structural and textural similarities.

CONCLUSION

This investigation highlights the following points:

(i) Ruthenium catalysts prepared in a highly dispersed state by cationic exchange or anionic adsorption on active carbon extrudates are very active for glucose hydrogenation (initial specific activities 1.1 mol h^{-1} g_{Ru}^{-1} at 100°C). The true activity of ruthenium should even be higher since under the present reaction conditions internal and external mass transfer should limit the reaction rate. The activity measured with our catalysts was five times higher, for the same operating conditions, than that deduced from the rate law established by Germain *et al.* (5).

(ii) Comparison with kieselguhr-supported nickel catalysts studied previously (2) shows that the specific activities of ruthenium catalysts were ca. 50 times higher than those of nickel catalysts. In addition to its higher activity, ruthenium had the crucial advantage that, unlike nickel, it did not leach away in solutions. Active carbon was also much more stable in the slightly acidic and chelating reaction medium than oxide supports such as alumina used previously by Arena (6).

(iii) The activities of catalysts were very stable over a long period of time. A weak deactivation was observed for the catalyst prepared by ion exchange (3.7% for 312 h on stream) and an even smaller deactivation, if any, may occur for the catalyst prepared by anionic adsorption.

(iv) Selectivity to sorbitol higher than 99.2% can be obtained on all catalysts; the shorter the residence time, the higher the selectivity. The study pinpointed the negative effect of high residence time, which favors epimerization of sorbitol to mannitol. This consecutive reaction is minimized by maintaining a residence time close to the point at which 100% conversion is attained. In that respect, continuous reactors are much more convenient than the discontinuous process since the residence time can be adjusted very precisely to meet the above requirement.

REFERENCES

1. Gallezot, P., Cerino, P. J., Blanc, B., Flèche, G., and Fuertes, P., *J. Catal.* **146**, 93 (1994).
2. Déchamp, N., Gamez, A., Perrard, A., and Gallezot, P., *Catal. Today* **24**, 29 (1995).
3. Wisniak, J., and Simon, R., *Ind. Eng. Chem. Prod. Res. Dev.* **18**, 50 (1979).
4. Makkee, M., Kieboom, P. G., and van Bekkum, H., *Carbohydr. Res.* **138**, 237 (1985).
5. Germain, A. H., Wauters, M. L., L'Homme, G. A., and Lefèbvre, A. G., *in* "Proceedings 7th International Congress on Catalysis" (T. Seiyama and K. Tanabe, Eds.), Vol. B, p. 1492. Elsevier, Amsterdam, 1981.
6. Arena, B. J., *Appl. Catal. A General* **87**, 219 (1992).
7. Giroir-Fendler, A., Richard, D., and Gallezot, P., *in* "Heterogeneous Catalysis and Fine Chemicals" (M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier, and G. Perot, Eds.), p. 171. Elsevier, Amsterdam, 1988.
8. Gallezot, P., Chaumet, S., Perrard, A., and Isnard, P., *J. Catal.* **168**, 104 (1997).