

Synthesis and CO Hydrogenation Activity of Ruthenium Zeolite A

Joseph A. Rossin and Mark E. Davis

Department of Chemical Engineering
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Ruthenium zeolite A was synthesized by several techniques from either RuCl_3 or $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. An example of our synthesis procedure with RuCl_3 is described below. First, zeolite A is synthesized in the presence of RuCl_3 by simple addition of the ruthenium salt to a standard zeolite A synthesis gel. The resulting ruthenium-zeolite A was crystallized in approximately 2 hours under autogeneous pressure at 95°C . Next, a portion of the ruthenium-zeolite A was added to another zeolite A synthesis gel to serve as a "carrier" of ruthenium and as a "seed" for the synthesis. Ruthenium-zeolite A was recovered from the "seeded" synthesis and exchanged with CaCl_2 for the two reasons: (1) to remove exchangeable ruthenium from the surface of the zeolite (intrazeolitic ruthenium will be too large to exchange out of the α -cage), and (2) to place the zeolite A in its most stable form (the calcium form of zeolite A is more stable than NaA to attack by water at elevated temperatures). This RuCaA will be denoted catalyst B. For comparison, a CaA was ion exchanged with aqueous RuCl_3 and this RuCaA will be denoted catalyst A.

Table 1 shows the X.P.S. and bulk chemical analysis (C.A.) data for catalysts A and B. Notice that the X.P.S./C.A. ratio for ion exchanged RuCaA is 14.7 while that of our synthesized RuCaA is 0.22. Since the X.P.S./C.A. ratio gives an indication of the amount of ruthenium in the superficial region relative to that in the bulk, it is obvious that catalyst B contains intrazeolitic ruthenium.

Catalyst B was tested for CO hydrogenation activity. The catalyst was heated to 150°C in flowing He for several hours to partially dehydrate the zeolite before reduction. Next, this material was exposed to flowing H_2 at 275°C , 2.25 atm. in order to reduce the ruthenium. Finally, 1:1 $\text{CO}:\text{H}_2$ was contacted with the catalyst at 255°C , 2 atm. (2.1 g catalyst, $F = 6.5$ ml/min).

Figure 1 shows the start-up behavior of catalyst B. Notice that the production of all hydrocarbons other than C_2 proceeds through a maximum. Also, these maxima do not occur at the same time. Figure 2 illustrates the hydrocarbon product distribution for over 10 hours of contact with syngas. In no case were branched hydrocarbons or hydrocarbons of C_8 (only traces of C_6 and C_7) or greater observed in the product stream (see Table 2 for an example of an exact product distribution).

X-ray diffraction analysis of catalyst B following reaction showed no loss in crystallinity, however, a 22% loss in pore volume (by O_2 adsorption) was observed. The loss in pore volume could be due to adsorbed hydrocarbons, structural rearrangements of the zeolite, or a combination of both factors. The FTIR spectrum of catalyst B after exposure to reaction conditions did show new bands in the zeolite framework region. These alterations suggest that changes in the zeolite have occurred over the course of the reaction. X.P.S. analyses of catalyst B: (i) as synthesized, (ii) after H_2 exposure, and (iii) after reaction show that the ruthenium was reduced by the H_2 and that during the course of the reaction the ruthenium did not migrate to the surface of the zeolite.

Table 1
XPS and Chemical Analysis Data for RuCaA

Catalyst	wt.%Ru	Ru/Si			Preparation
		XPS	CA	XPS/CA	
A	1.98	0.534	0.0363	14.7	exchange
B	1.53	0.006	0.0276	0.22	synthesis

Table 2
Product Distribution for RuCaA (Catalyst B).
T = 255°C, P = 2 atm, CO:H₂ (1:1), t = 3.5 h

Hydrocarbon	Mole Percent	Weight Percent
Methane	66.09	36.17
Ethane	2.00	2.19
Ethylene	2.00	2.19
Propane/Propylene	13.30	21.84
1-Butene	0.43	0.95
n-Butane	2.98	6.52
t-2-Butene	7.08	15.15
c-2-Butene	3.65	7.80
n-Pentane	2.48	6.80

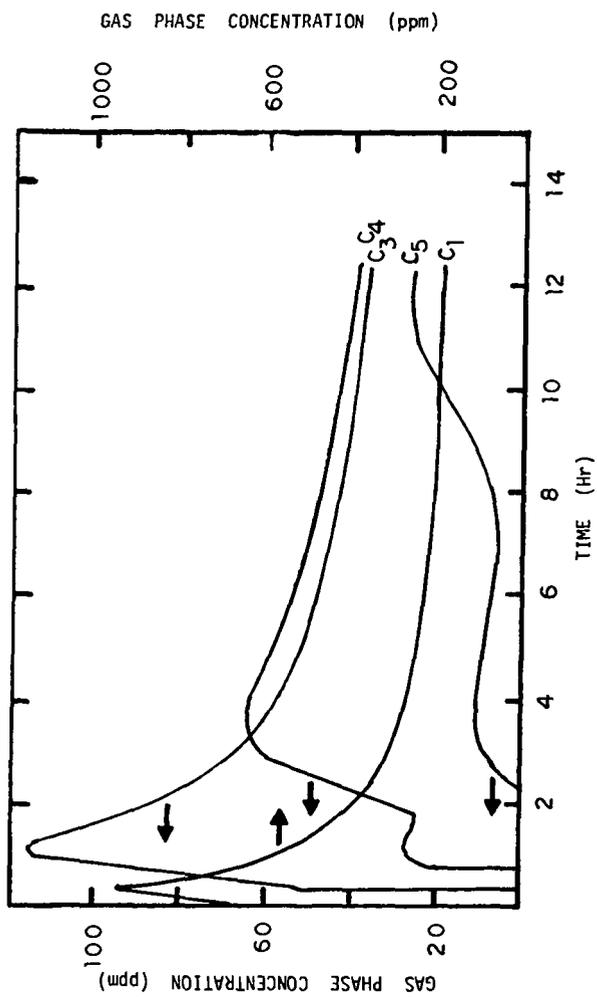


Figure 1: Hydrocarbon Product Start-up Behavior for Catalyst B at 255 C. All hydrocarbons were linear.

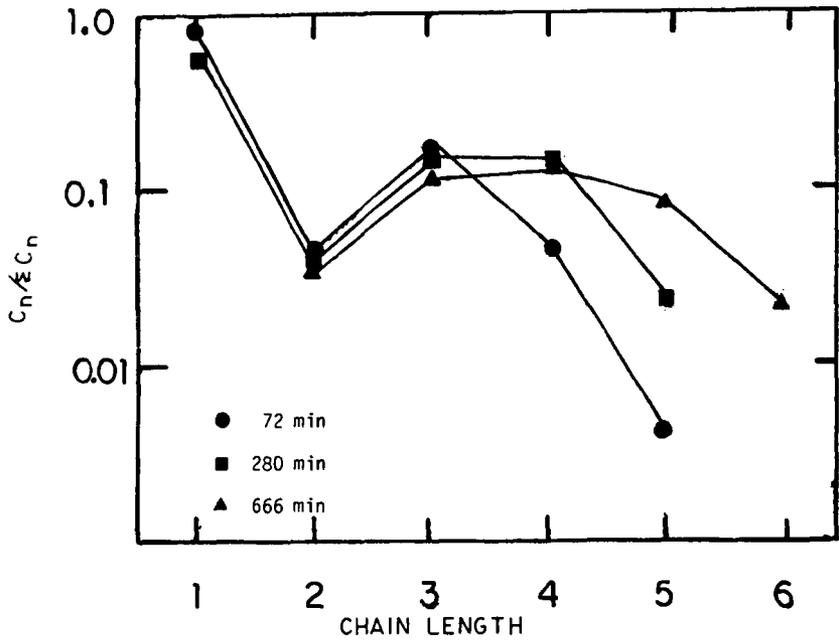


Figure 2: Hydrocarbon Product Distribution for Catalyst B at 255 C. All hydrocarbons were linear.