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Aromatization of *n*-Hexane by Pt Clusters Supported on High Surface Area MgO

Light naphtha containing mostly C_6 and C_7 molecules is an important constituent of motor gasoline but has a rather low research octane rating of 45–70 (*1*). Conventional hydrocarbon reforming catalysts used for improving the octane rating of C_8–C_{10} hydrocarbons are not effective for upgrading light naphtha so tetraethyl lead antiknock compounds are added instead. The gradual phase out of leaded gasoline has therefore stimulated research in the area of light naphtha reforming.

The octane number of straight chain hydrocarbons is increased by aromatization and isomerization to branched hydrocarbons. Typical reforming processes use catalysts composed mainly of noble metal clusters supported on an acidic carrier like Al_2O_3, but the selectivity of these catalysts for conversion of hexanes and heptanes is poor. The mechanism for reforming on these materials is bifunctional: the noble metal provides a dehydrogenation–hydrogenation site and the acidic support catalyzes structural rearrangements of the hydrocarbon chains (*2*).

Recently, platinum clusters inside the unidimensional channel structure of zeolite L were found to catalyze the aromatization of hexane and heptane with exceptionally high activity and selectivity (*1, 3, 4*). A drawback of this catalyst is its high sensitivity to sulfur poisoning, thereby demanding hydrocarbon feedstocks of high purity (*1*). The absence of acidity in the Pt-zeolite L and the correlation of reaction rate with Pt loading suggest that this catalyst is monofunctional, depending solely on Pt metal for the catalytic function. However, the activity and selectivity for aromatization are improved when the zeolite is exchanged with cations that increase the basicity of the zeolite support (*5*). This points to a significant role of the support on the desired catalytic reaction by either modifying the atomic or electronic structure of the Pt clusters or through direct participation of support sites in the reaction mechanism. Evidence for a metal–support interaction between Pt clusters and the cations of zeolite L was reported by Larsen and Haller who measured changes in the ratio of the toluene to benzene adsorption equilibrium constant on Pt after exchanging zeolite L with various alkaline earth cations (*6*).

Early work with Pt-zeolite based materials (mordenite, omega, X, Y, and L) showed that zeolite L was the most selective support for aromatization of *n*-hexane (*3*). Tauster and Steger propose that the unidimensional channels of zeolite L collimate the diffusing flux of *n*-hexane molecules so that their long axis is parallel to the zeolite channel (*7, 8*). The high selectivity observed for a zeolite L catalyst may result from end-on or terminal adsorption to the Pt surface. A molecular graphics study of hydrocarbon interactions with a Pt cluster inside a channel of zeolite L revealed that *n*-hexane has adequate space to curve around on itself with both ends attached to a single Pt atom (*9*). It was suggested that the spatial limitations within the zeolite L channel maximize the Van der Waals interactions of the curved hydrocarbon with the channel walls, which leads to a stabilized cyclic intermediate.

The surface structure of the Pt cluster has also been suggested to affect aromatization selectivity. Platinum clusters supported on carbon were shown to selectively catalyze

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n-hexane aromatization when the clusters were promoted by sodium ions (*10, 11*). The enhanced selectivity to benzene formation was attributed to Na^+ promoting a structural rearrangement of the Pt cluster analogous to surface restructuring that has been observed previously by low energy electron diffraction of alkali metals on well-defined Pt single crystals. Results from the single crystal work suggested that the promoter ions induce a reorientation of the outer layer of Pt atoms to form a hexagonal (111) surface layer which was postulated to be the active, selective, Pt atomic arrangement for the aromatization reaction (*10, 11*).

In the work presented here, we elaborate on our earlier report dealing with the dehydrocyclization of *n*-hexane to form benzene over Pt clusters supported on a high surface area, magnesium oxide carrier (*12*). A nonzeolitic support with no analogous channel or cage structure was chosen to minimize the Van der Waals interactions of the surrounding environment on the reactivity of *n*-hexane. In addition, acid-catalyzed isomerization and cracking side reactions known to occur on conventional reforming catalysts should be suppressed due to the basicity of MgO.

A stabilized high surface area MgO support was prepared by coprecipitation of Mg and Al nitrates in a 5 : 1 Mg : Al molar ratio in the presence of KOH and K_2CO_3 (*13*). Nitrates were used instead of sulfates to avoid poisoning of the Pt by S in the finished reduced catalyst. The resulting hydroxycarbonate (hydrotalcite structure confirmed by X-ray diffraction) was decomposed in air at 873 K for 12 h. The specific surface area of the final stabilized magnesia as determined by N_2 adsorption using the BET formulation was 220 m^2 g^{-1}. This stabilized magnesia was then impregnated wih an aqueous solution of $Pt(NH_3)_4Cl_2$ (Johnson Matthey Specpure), dried, and calcined in air at 650 K for 6 h to give a 0.88 wt.% (determined by ICP emission analysis) Pt sample designated as Pt/Mg(Al)O. The calcined material was reduced in flowing H_2 at 700 K for 2 h. A zeolite L catalyst, Pt/KL, was also prepared for comparison. Zeolite L in the potassium form (Linde) was ion exchanged with aqueous $Pt(NH_3)_4Cl_2$, washed, dried, calcined, and reduced according to the above procedure for the magnesia sample to give a final Pt loading of 0.52 wt.%.

Dihydrogen adsorption isotherms were measured at room temperature (RT) in a standard, static, volumetric adsorption apparatus and were used to calculate the fraction of Pt atoms exposed to the surface. The linear part of the adsorption isotherm was extrapolated to zero pressure to obtain the number of hydrogen atoms associated with the metal surface. Before measuring an isotherm, a sample was first reduced in flowing H_2 at 700 K for 2 h and evacuated at that temperature for 1 h before cooling to room temperature in vacuum. A backsorption isotherm was also measured after evacuating the sample for 0.5 h at RT.

Both the magnesia and zeolite catalysts were tested in a single pass, quartz, tubular reactor (4-mm i.d.) for the steady state conversion of *n*-hexane at 750 K and atmospheric total pressure (40 kPa H_2, diluent He) with a ratio of H_2 to hydrocarbon of six. The catalyst powders were pressed without binder into pellets, then crushed and size separated to give catalyst grains between 0.25 and 0.50 mm in diameter. Helium (Air Liquide, 99.99%) and electrolytically generated dihydrogen (Milton Roy) passed through MnO–silica indicators to show the absence of oxygen in the gas streams before mixing and entering a double saturator containing *n*-hexane (Merck, 99.0%) at 273 K. The reactant stream then passed over a vertical catalyst bed heated by a tubular furnace. Product gases were analyzed by online gas chromatography. A typical run consisted of loading about 300 mg of catalyst into the reactor and re-reducing the Pt *in situ* with flowing H_2 at 700 K for 2 h before introducing He and the reactant *n*-hexane. The steady state reaction was carried out for 0.5 h at 700 K before increasing to the standard temperature of 750 K. Contact times were based on the number of hexane molecules passing through the catalyst bed

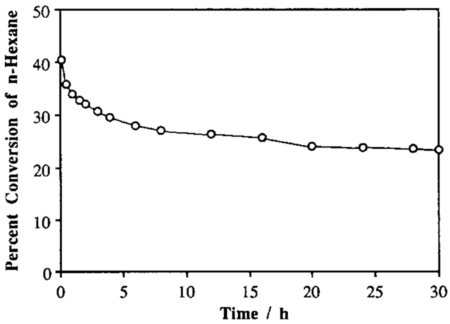

FIG. 1. Deactivation of Pt/Mg(Al)O during reaction of *n*-hexane at standard conditions and contact time of 3.5 s.

per surface Pt atom per second. For proper comparison, the number of surface Pt atoms in the reactor was the same for each run and all results were obtained after at least 1 h on stream unless otherwise stated. The selectivity for a specific reaction product is determined by the fraction of *n*-hexane converted to that product and is expressed in percent.

The ratio of adsorbed H atoms to Pt atoms at RT was measured to be 0.49 for Pt/Mg(Al)O and 1.0 for Pt/KL. Since the stoichiometry of adsorbed H atoms to surface Pt atoms is about 1 : 1 (*14*), the fraction of Pt metal exposed is equal to the above H/Pt ratios. Backsorption isotherms measured for both samples showed that 25–30% of the hydrogen could be removed from the surface after evacuation for 0.5 h at RT. Therefore, the number of surface Pt atoms were measured by the total uptake of H_2 at RT extrapolated to zero pressure. It should be noted that the uptake of dihydrogen on the magnesia catalyst increased unexpectedly at about 25 kPa for both the bare Pt and backsorption isotherms. However, the adsorption isotherm for Pt/KL was linear over the entire range of pressures used (5–30 kPa).

The conversion of *n*-hexane was nearly the same for each catalyst over the range of contact times studied (*12*). Since contact time was based on the flow rate of *n*-hexane and the quantity of surface Pt atoms into the reactor, the overall reaction rate per surface Pt atom was independent of support. An interesting result is that the magnesia catalyst competes with the zeolite catalyst in terms of benzene selectivity at our conditions (*12*). A comparison of the selectivity to other products for the magnesia and zeolite catalyst at about 40% conversion is reported in Ref. (*12*). In classes of products formed by aromatization, cyclization, isomerization, and dehydrogenation, the selectivity was about the same. A carbon material balance with methane internal standard demonstrated that the reported products accounted for more than 99% of the products formed in the reaction.

We attempted to decrease residual acidity resulting from the initial reduction of Pt ions by back-exchanging a Pt/KL sample with aqueous Ba^{2+} ions. This sample was then dried, calcined in air at 650 K for 6 h, and re-reduced in H_2 at 700 K for 2 h. Treating the sample at these conditions allows for migration of Ba^{2+} out of the main channel into a locked position (*15*). Chemisorption of hydrogen revealed a negligible change of particle size after back-exchange, which is consistent with previous work on the Pt–L system (*6*). This material was tested in the aromatization of *n*-hexane at standard conditions, and no improvement in activity or selectivity to benzene was observed.

A reaction run was carried out for 30 h to test the stability of the Pt/Mg(Al)O catalyst. After the usual re-reduction step in H_2 at

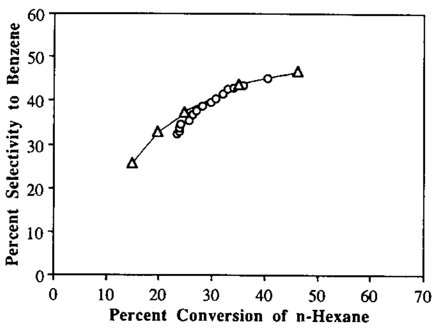

FIG. 2. Influence of conversion on the selectivity to benzene during *n*-hexane reaction at standard conditions. Circles correspond to data from the deactivation experiment and triangles correspond to data from different contact times (see Ref. (*12*)).

700 K for 2 h, the reactant stream was introduced at 700 K for 0.5 h. The results in Fig. 1 show the time evolution of *n*-hexane conversion where the origin corresponds to the time at which the reactor temperature was raised to 750 K. The catalyst deactivated after 30 h to a level of about 60% of its initial activity with most of the change occurring in the first 5 h of reaction. The selectivity to benzene formation also decreased with time. Figure 2 shows a comparison of the selectivity to benzene formation over Pt/Mg(Al)O for different levels of *n*-hexane conversion determined by contact time and deactivation. The data points from the deactivation experiment overlap the data from varying the contact time demonstrating that the deactivation does not alter the intrinsic selectivity of the catalyst.

Chemisorption of hydrogen onto the surface of the Pt clusters was used for a simple determination of the average cluster size. We chose H_2 instead of CO as a probe molecule based on the results of Larsen and Haller, who reported a significant variation in the adsorption capacity of CO after exchanging the zeolite cation in various Pt–L catalysts whereas the H_2 adsorption capacity remained unaffected (*6*). Results for our zeolite catalysts (H/Pt = 1.0) showed that nearly every Pt atom was exposed to the surface. Therefore, the average cluster diameter is about 1 nm, which is small enough to fit inside the unidimensional channel structure of zeolite L. Reaction rates over this catalyst were calculated assuming every Pt atom was potential catalytic site. Results for Pt/Mg(Al)O (H/Pt = 0.49) suggest that the Pt clusters are about 2 nm in average diameter or twice as large as the zeolite-supported Pt clusters. As mentioned earlier, the uptake of dihydrogen on the magnesia sample at pressures in excess of about 25 kPa was greater than can be accounted for by simple physisorption. Dihydrogen is evolved at high temperatures from the dissociation of surface hydroxyl groups on magnesia (*16*). The uptake of H_2 on our magnesia could result from the reverse process of hydroxyl formation at RT (*17*). Activation of dihydrogen on magnesia at low temperatures was demonstrated by Boudart *et al.* who reported that the H_2–D_2 exchange reaction is catalyzed by MgO at 78 K (*18*). The formation of hydroxyl groups may in fact be enhanced by the presence of Pt clusters which can readily dissociate dihydrogen at RT and spill over atomic hydrogen to the support. If at lower pressures some hydrogen is strongly adsorbed on the Mg(Al)O then we may *overestimate* the actual H/Pt ratio. In that case, the observed rates of reaction will be even greater per surface Pt atom and our overall conclusions remain unaffected.

The main result of this work is the similarity of the zeolite and non-zeolite Pt catalysts in terms of activity and selectivity for the aromatization of *n*-hexane (see Ref. (*12*)). The difference in metal cluster sizes for the two catalysts appears to have no effect on the rate or selectivity of *n*-hexane reactions. However, the Pt particle size during the aromatization reaction may be greater than the size calculated from hydrogen chemisorption since the reaction temperature (750 K) is higher than the reduction temperature before chemisorption (700 K). Even if the particles were larger during reaction than estimated from chemisorption, our conclusions that are based on selectivity as a function of total conversion are the same. In addition, transmission electron micrographs of the catalyst after reduction and after reaction showed Pt particle sizes consistent with H_2 chemisorption.

The low production of hexane isomers in both cases suggests the lack of significant acidity of the support magnesia and zeolite. Previous work verified that incorporation of Al does not alter the pronounced basicity of magnesium oxide (*13*). However, reduction of Pt^{2+} cations in the zeolite by hydrogen induces residual acidity. We have therefore ion exchanged a previously reduced Pt/KL zeolite with aqueous Ba^{2+} in an attempt to decrease acidity resulting from the reduction process. Barium was used since the large cation increases the basicity of zeolite L and a Pt/Ba zeolite L was reported earlier to be an excellent catalyst for aromatization of *n*-hexane (*4*). We observed no improvement in the catalyst performance at our conditions after ion exchange with Ba^{2+}. Therefore, the comparison of Pt/Mg(Al)O to Pt/KL appears to be unaffected by the residual acidity introduced by reduction. Perhaps the relatively few protonic sites created by exchange and reduction do not play a significant role in the observed catalysis. Bernard has demonstrated that Pt–L catalysts prepared without the formation of protonic sites are more selective to benzene formation but the increase in selectivity is small (*3*). Our result is not in agreement with an earlier report which demonstrates that ion exchange of heavy cations into zeolite L increases the activity and selectivity of supported Pt (*5*). In this work the heavy cation was back-exchanged *after* the Pt clusters were formed, whereas the zeolites in Ref. (*5*) were exchanged *before* Pt incorporation. In principle, the method of Ba^{2+} incorporation should not be important but the order of cation exchange and Pt cluster formation apparently influences the properties of the final catalyst.

For the Pt/Mg(Al)O system, no channel or cage structure analogous to a zeolite exists. We can therefore rule out any influence of spatial constraints on the stabilization of a cyclic intermediate as has been proposed for the zeolite case (*9*). Although the Mg(Al)O support may be acting as an inert carrier for the Pt particles, based on a recent literature report (*6*) it appears more likely at this moment that the basic properties of the support could influence directly the electronic properties of the metal clusters. Therefore, a metal–support interaction may account for the observed selectivity to benzene.

Another possibility can also explain our results. The aromatization mechanism may be bifunctional where surface basic sites on the magnesia support supplement the catalytic sites of the Pt clusters. Paal has reviewed results from ^{14}C radiotracer studies and temperature programmed desorption of *n*-hexane and possible intermediates in the dehydrocyclization reaction (*19*). Much of the evidence points to stepwise dehydrogenation of *n*-hexane on Pt to form hexenes, dienes, and trienes, which subsequently undergo cyclization and aromatization. The cyclization step has been proposed to occur over monofunctional Pt catalysts by both Pt-catalyzed ring closure and thermal cyclization of hexatrienes (*20*). In addition, the importance of internal olefins during hexane reactions over a Pt-zeolite L has been suggested recently (*21*). We propose that benzene may be produced by Pt-catalyzed dehydrogenation of *n*-hexane followed by the reaction of hexenes, dienes, and trienes, to form aromatics on the support basic sites or on the Pt metal. However, we cannot rule out a contribution of thermal cyclization of hexatrienes in our system based on the work of Lewis and Steiner who showed that hexa-1,*cis*-3,5-triene cyclizes in the gas phase at a much lower temperature than was used here (*22*). The function of MgO in the proposed scheme is supported by the work of Suzuka and Hattori who demonstrated recently that 1,3-butadiene can dehydrocyclodimerize to form ethylbenzene and o-xylene over MgO at 473 K (*23*). The specific details of base catalyzed hydrocarbon reforming reactions are not well understood and will not be discussed. They will be dealt with in future work.

We also investigated the stability of the magnesia catalyst by carrying out the reaction for 30 h at 750 K. Deactivation that occurred in the first 5 h accounted for most of the loss of catalytic activity (Fig. 1). However, the catalyst appeared quite stable at later time. Initial deactivation of the catalyst may have resulted from agglomeration of Pt during reaction which decreased the available metal surface area but this was not readily apparent from TEM results. The selectivity to benzene formation varied with *n*-hexane conversion in the same way regardless of conversion being altered by adjusting the contact time or by deactivation (Fig. 2). This observation is consistent with some Pt agglomeration during reaction. However, another reason for deactivation may be deposition of an unreactive carbonaceous layer on the catalyst surface during the initial stages of reaction. This unreactive carbon layer, however, must poison all sites equally since the selectivity of the reaction is unchanged.

Platinum clusters supported on stabilized magnesia catalyzed the aromatization of *n*-hexane with nearly the same activity and selectivity to benzene as a reference Pt-zeolite L, thereby demonstrating that high surface area basic supports can function advantageously in hydrocarbon reforming reactions. This is further supported by the long time stability of Pt/Mg(Al)O. After an initial decline in activity, the magnesia catalyst appeared stable toward additional deactivation. The aromatization of *n*-hexane over Pt/Mg(Al)O may occur through a bifunctional mechanism where the metal sites dehydrogenate *n*-hexane and the support basic sites catalyze cyclization and aromatization. The activity and selectivity for aromatization over Pt-Mg(Al)O suggest that geometric interpretations may not completely explain the catalysis observed over zeolite materials.

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