Oxygen effect on the selectivity of ketone hydrogenation reaction on Pt and Pd catalysts

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An oxygen deactivated metal catalyst that exhibits less catalytic activity can catalyze an extensive ketone hydrogenation reaction which results in the formation of alkanes, but a fully reduced metal catalyst that exhibits stronger catalytic activity only catalyzes a mild hydrogenation reaction which results in the formation of alcohols.

Keywords: oxygen effect; ketone; hydrogenation; Pd

Control of the reaction selectivity of carbonyl groups has been the subject of a number of investigations. Although the reaction of carbonyl compounds on metal surfaces has been intensively studied, little agreement upon the interpretation of reaction selectivity has been reached [1–8].

Acetone is the simplest carbonyl compound and it is a common model for studying the reaction of carbonyl compounds on metals. Isopropanol and propane are the two primary products of the hydrogenation of acetone over transition metals. The reaction product observed on most of the supported metal catalysts is isopropanol with near 100% selectivity. Propane is formed in detectable amounts on Pt foils, Pt films and unsupported Pt powders. A lesser extent of propane is produced over other unsupported transition metal surfaces. No propane formation was reported on Pd and Au catalysts [8]. However, we have found that propane can be formed on SiO_2 supported Pd and Pt catalysts when oxygen is present in the acetone hydrogenation reaction system. A similar phenomenon is observed when acetone was replaced by other ketones. It is surprising that an oxygen deactivated metal catalyst that exhibits less catalytic activity would catalyze an extensive hydrogenation reaction, which results in the formation of propane. But a fully reduced metal catalyst that exhibits stronger catalytic activity only catalyzes a mild hydrogenation reaction, which results in the formation of isopropanol. In this study, we use gas phase ketone hydrogenation on Pt and Pd/SiO_2 as a model to reveal the oxygen effect on the selectivity of carbonyl group hydrogenation reaction.

A 4.7 wt% Pt/silica catalyst and a 2.6 wt% Pd/silica catalyst were prepared by impregnating Cab-O-Sil M-5 SiO_2 with an aqueous solution of H_2PtCl_6 or a 4 M HCl aqueous solution of $PdCl_2$. The catalyst was dried at 80°C and calcined in flowing air at 250°C for 5 h before the reduction treatment. Hydrogen (Sun-Fu Gas Co., 99.99% pure) and nitrogen (Sun-Fu Gas Co., 99.999% pure) was further purified by passing it through a deoxo purifier. Ketone compounds were degassed with multiple freeze–pump–thaw cycles. Oxygen was used without any further purification.

Ketone hydrogenation was carried out in a fixed bed reactor system with a 0.5% H_2/N_2 gas at 25°C and an atmospheric pressure. Samples of 10–20 mg catalyst were reduced in flowing H_2 for 10 h at the described temperatures. The temperature was ramped from room temperature to a desired reduction temperature at a rate of 10°C/min. The average particle size of the supported Pt and Pd after this treatment, estimated by X-ray line broadening, is about 80 and 160 Å, respectively. Ketones were introduced into the reactor system by a calibrated 0.5 cm^3 syringe pump. The ketone/H_2/N_2 feed streams were passed over the catalysts for 30 min before a sample was taken for analysis. The catalysts were purged with H_2/N_2 for 30 min between each ketone/H_2/N_2 exposure to maintain the catalytic activity. The gas flow rates were measured by a MKS 1259 flow controller. The flowing system of the reactor was heated with heating belts to avoid the condensation of samples.

The conversion of ketone in the hydrogenation reaction was typically kept below 10% to avoid heat and mass transfer effects and to keep the reaction in differential mode to ensure interpretable analysis of the data. The products were analyzed by a gas chromatograph (Shimadzu GC-8A) with a 6 foot FFAP column. Product concentrations were determined with a Shimadzu CR-6A integrator by comparing the peak areas to those for a standard mixture.

The effect of oxygen on the selectivity of the acetone hydrogenation reaction is demonstrated in fig. 1. The propane formation rate increases with increasing the

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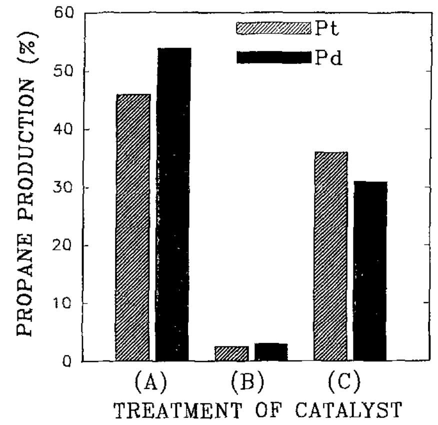

Fig. 1. Hydrogenation of acetone to propane at 25°C on (A) oxygen calcined catalysts (without reduction pretreatment); (B) 400°C reduced Pt and 300°C reduced Pd catalysts; (C) following (B) and then dosed with 60 ml of oxygen at room temperature. The flowing rate of 0.5% H_2/N_2 = 100 ml/min. The molar ratio of acetone/H_2 = 1/2.

oxygen dosage on the catalyst. Isopropanol is produced with near 100% selectivity when the reaction is catalyzed by fully reduced catalysts. Around 50% of propane production is observed when acetone hydrogenation is catalyzed by a fully oxidized Pd or Pt catalyst (without reduction pretreatment). Note that the oxidized surface Pd and Pt atoms can be reduced by the hydrogen in reactant streams at room temperature. Temperature programmed reduction investigations demonstrate that the surface Pd and Pt oxide can be reduced to Pd and Pt at temperatures between 200 and 400 K [9,10]. It is difficult to monitor the hydrogenation reaction on a truly fully oxidized metal catalyst at room temperature. The lower propane formation rate on a room temperature reduced Pd catalyst as compared with that on a Pt catalyst is due, at least partially, to the higher reducibility of the Pd catalyst at room temperature.

The enhancement of propane formation from the acetone hydrogenation reaction by oxygen perturbed Pd and Pt catalysts is a general phenomenon that can be extended to increase the selectivity toward methylene group formation from ketone hydrogenation reactions. Table 1 shows the methylene formation percentage from the hydrogenation reaction of some ketones catalyzed by oxidized Pd catalyst. A significant enhancement of the methylene group formation rate is observed on an oxygen perturbed Pd catalyst. This behavior is more pronounced when an aromatic substituent ligand exists in the ketone compounds. Previous studies concerning the hydrogenation of α,β-unsaturated aldehydes have shown that sulphur does not influence Pt catalysts but significantly enhances the selectivity for the unsaturated alcohol on Cu catalysts [11,12]. Oxygen and sulphur are in the same group of the periodic table. We therefore also checked the effect of oxygen on the benzaldehyde hydrogenation reaction. The major product of the benzaldehyde hydrogenation on Pd and oxidized Pd/SiO_2 catalyst is toluene. Oxygen does not influence the Pd catalyst for benzaldehyde hydrogenation reaction.

Fig. 2 illustrates the variation of methylene group formation rate versus the conversion of ketones at room temperature on oxygen perturbed Pd and Pt catalysts. A non-zero extrapolated value of the methylene group formation rate to zero conversion of ketones is observed. This result suggests that alcohols are not necessary to be an intermediate for the production of alkanes from ketones. The formation of alkanes and alcohols on oxygen perturbed metal catalysts may be controlled by a parallel reaction path.

Ayre and Madix studied reactions of atomic oxygen with acetone on Ag(110) and found that the C–H bond scission can be activated by the adsorbed oxygen to produce $OH_{(a)}$ and acetone enolate ($CH_2{=}C{-}(CH_3)O_{(a)}$) [13]. The hydroxyl disproportionation reaction on the Ag(110) surface occurs at temperatures of about 300 K.

The mechanism of propane formation catalyzed by oxygen perturbed metal catalysts may relate to the formation of adsorbed acetone enolate species. An aromatic substituent ligand in the ketone may facilitate the enolation process. The positive effect of the phenyl group on the methylene group formation (see table 1) provides evidence for the above hypothesis.

Friedman et al. conducted a deuterium exchange reaction accompanied with the reduction of acetone. They found that the peak of the mass distribution of the polydeuteropropanes was 46 amu ($C_3H_6D_2$) [2]. This would support the above hypothesis through the following reaction schemes:

Table 1
Effect of oxygen on the formation of methylene and hydroxyl groups from ketones on Pd catalysts [a]

Ketones	Oxidized Pd/SiO_2			Reduced Pd/SiO_2		
	$-CH_2-$	–OH	conversion	$-CH_2-$	–OH	conversion
CH_3COCH_3	54	46	4	3	97	3
$C_6H_5COCH_3$	96	4	8	30	70	5
$C_6H_5CH_2COCH_3$	94	6	6	6	94	3
$C_6H_5COC_2H_5$	96	4	7	2	98	4

[a] $-CH_2-$ = (methylene group formation/all products) ×100, –OH = (hydroxyl group formation/all products) ×100, conversion = ($\text{ketone}_{in} - \text{ketone}_{out}/\text{ketone}_{in}$) × 100. The flowing rate of 0.5% H_2/N_2 was 100 ml/min. The molar ratio of ketone/H_2 = 1/2.

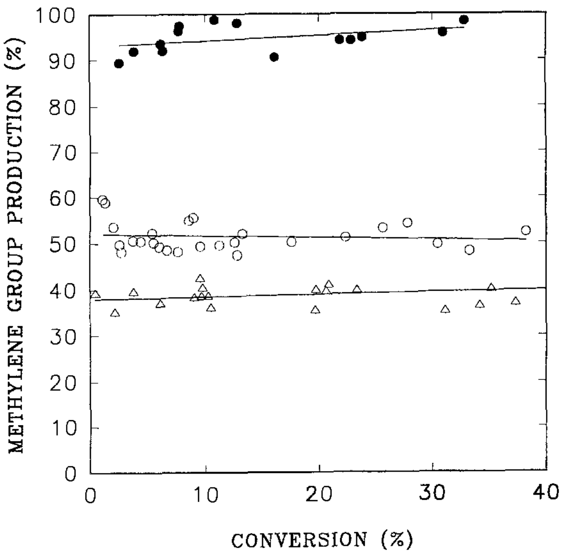

Fig. 2. Plot of the methylene group formation rate variation versus the conversion of ketone in the hydrogenation reaction at 25°C on oxygen perturbed catalyst. (●) Ethylbenzene from acetophenone hydrogenation on oxidized Pd/SiO_2 (without reduction pretreatment), (○) propane from acetone hydrogenation on oxidized Pd/SiO_2 (without reduction pretreatment), (△) on room temperature reduced Pt/SiO_2. The flowing rate of 0.5% H_2/N_2 was varied from 20 to 200 ml/min. The molar ratio of ketone/H_2 = 1/2.

$$CH_2{=}C(CH_3){-}O_{(a)}\cdots HO_{(a)} + nD_2 \rightarrow C_3H_6D_2 + O_{(a)} + D_2O$$

Four D atoms would be introduced into the propane molecule when isopropanol was involved in the propane formation process [2]. This result also suggests that the formation of propane and isopropanol from acetone on oxygen perturbed metal catalyst can be controlled by a parallel path.

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