

Fourier Transform Infrared Spectroscopic Study on the Adsorption of Ethyl Pyruvate on Pt/ γ -Al₂O₃: Side Reactions Suppressed by Adsorbed Hydrogen and Cinchonidine

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Adsorption and reaction of ethyl pyruvate (EtPy), a model reactant in chiral hydrogenation of α -ketoester on Pt/ γ -Al₂O₃ were studied by IR spectroscopy. In vacuum and Ar flow at room temperature, several side reactions of EtPy are detected by IR spectroscopy: decomposition on Pt, aldol condensation, and hydrolysis on γ -Al₂O₃. When the quantity of adsorbed EtPy is small, CO formed from EtPy decomposition on Pt can react with the hydroxyl groups of Al₂O₃ to generate formate species. It is very interesting to find out that H₂ not only acts as a reactant for the hydrogenation reaction but also plays an important role in suppressing the side reactions of EtPy on Pt/ γ -Al₂O₃ catalysts. The suppressing effect of H₂ is not observed on γ -Al₂O₃ alone. The function of spilt-over H atoms in suppressing these side reactions was confirmed and discussed. Adsorbed cinchonidine (CD) alone cannot suppress the condensation and hydrolysis of EtPy on γ -Al₂O₃, but the decomposition of EtPy on Pt can be suppressed by adsorbed CD. The coexistence of CD and H₂ thoroughly inhibits all of these side reactions of EtPy on Pt/ γ -Al₂O₃. Adsorbed CD can help hydrogen to avoid site-blocking with side-reaction products then facilitate hydrogenation on Pt, which may be a reason for the rate acceleration effect of the adsorbed CD.

1. Introduction

Heterogeneous chiral catalysis is a subject of increasing interest in both the scientific and industrial communities due to its intrinsic technical advantages including easily handling, separation, and regeneration.^{1–5} The asymmetric hydrogenation of α -ketoesters on Pt modified with cinchonidine (CD) or other cinchona alkaloids is the subject of intense current study.^{6–11} Cinchona alkaloids on platinum surface can induce enantioselective hydrogenation and show a rate acceleration effect. Considerable efforts have been made to achieve higher enantioselectivity and to extend the scope of effective chiral modifiers.^{11–15} By optimizing the reaction conditions, an enantiomeric excess (ee) of over 95% can be attained for the chirally modified Pt catalyst.^{15,25} The behavior of this catalytic system is sensitive to the introducing sequence of the reactants (methyl pyruvate, hydrogen) and modifier, as demonstrated earlier by transient kinetic measurements.¹⁶ The great challenge posed by this reaction arises from the fact that mutually interactive factors of the metal surface, the α -ketoester, the modifier, the solvent, and hydrogen with high pressure must be taken into account.

In addition to asymmetric hydrogenation, ethyl and methyl pyruvate undergo several side reactions both in solution and on the surface of Pt catalysts depending on the reaction conditions. In the presence of cinchonidine in solution, aldol reaction¹⁷ and hydrolysis¹⁸ of EtPy occurs. It was found that in vacuum, methyl pyruvate is polymerized to long-chain molecules on Pt{111} surface when the ratio of adsorbed H atoms to adsorbed α -ketoester is very low.^{8,19} On Pt^{20,21} and Ni,^{22,23} selective C–C bond scission of alkyl pyruvates generates CO

and other smaller hydrocarbon fragments. Most recently, attenuated total reflection infrared (ATR-IR) studies revealed that γ -Al₂O₃ catalyzed aldol condensation and hydrolysis of ethyl pyruvate (EtPy) when H₂-saturated CH₂Cl₂ was used as the solvent.²⁴ Side reactions occurring on both Pt and Al₂O₃ can lead to the blockage of the active Pt surface by fragmentation and polymerization products. Murzin et al. also suggested that side reactions of EtPy caused catalyst deactivation, which reduces the activity of the racemic reaction.¹⁰ Interestingly, acetic acid, the most suitable solvent for the enantioselective hydrogenation of ethyl pyruvate, was found to suppress the side reactions, adding a new facet to the beneficial role of this solvent.²⁴ However, considerable conversion and enantioselectivity can be obtained in the absence of acidic solvent (such as ethanol, CH₂Cl₂, and toluene or without solvent).⁴⁷ It is not yet clear which species accounts for suppressing the side reactions of adsorbed pyruvate on supported Pt catalysts in the absence of acidic solvent.

In this work, we investigated the adsorption of EtPy on Pt/ γ -Al₂O₃ catalysts in the absence of solvent by IR spectroscopy. The decomposition, aldol condensation, and hydrolysis of EtPy on Pt/ γ -Al₂O₃ were detected in vacuum and in Ar flow. The acid–base sites on the γ -Al₂O₃ surface are found to be responsible for the aldol condensation and hydrolysis of EtPy. Differing from the experiments of Ferri et al.²⁴ where H₂ dissolved in CH₂Cl₂, we show that gas-phase H₂ can significantly suppress the decomposition and aldol condensation of EtPy and thoroughly inhibit its hydrolysis on Pt/ γ -Al₂O₃. While on γ -Al₂O₃, these effects are not observed. The decomposition of EtPy on Pt can be suppressed in the presence of CD. Adsorbed CD alone cannot suppress the aldol condensation and hydrolysis of EtPy on γ -Al₂O₃, but CD can help H₂ thoroughly

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inhibit all these side reactions on Pt/ γ -Al₂O₃. The mechanism of hindering side reactions by adsorbed hydrogen and CD is discussed.

2. Experimental Section

2.1. Materials. γ -Al₂O₃ (Belgium, 210 m²/g) was calcined at 773 K for 3 h before use. SiO₂ (Degussa, 200 m²/g) was calcined at 873 K for 5 h before use. Hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O), cinchonidine (Acros, >98%), and organic solvents were AR grade and used as received. EtPy (Alfa Aesar, >98%) was further purified by freeze–thaw cycles in the gas-handling line. H₂ and Ar with purities of 99.999% were further purified by passage through oxygen/moisture traps to remove traces of oxygen and water.

2.2. Catalyst Preparation. The supported Pt catalysts with nominal metal loadings of 5.0 wt % were prepared via incipient wetness impregnation on γ -Al₂O₃ and SiO₂ using H₂PtCl₆·6H₂O as the precursor. Following the impregnation, all the catalysts were dried overnight at 393 K. γ -Al₂O₃-supported Pt catalyst was calcined for 2 h at 623 K and then reduced in sodium formate solution at 363 K.²⁵ SiO₂-supported Pt catalyst was calcined for 2 h at 523 K and then reduced in H₂ for 2 h at 573 K.

2.3. Fourier Transform IR (FTIR) Spectroscopy. All the IR spectra were collected on a FTIR spectrometer (Nicolet Nexus 470) with a resolution of 4 cm⁻¹ and 64 scans in the region of 4000–1000 cm⁻¹. Several IR experiments were performed as follows below.

2.3.1. EtPy Adsorption in Vacuum. The sample was pressed into a self-supporting wafer (ca. 15 mg/cm²) and put into a quartz IR cell equipped with CaF₂ windows. After treated in H₂ for 120 min at 673 K, it was evacuated on an ultrahigh vacuum system (10⁻³ Pa) at 723 K for 120 min and subsequently cooled to room temperature (RT). About 0.5 Torr (1 Torr = 133.33 Pa) of EtPy was introduced to the IR cell for EtPy adsorption at RT and subsequently evacuated for 2 min at RT. Closing the IR chamber, the IR spectra of adsorbed EtPy were monitored with time. After 10 h, the sample was evacuated at 373 K for 40 min. The IR spectrum was recorded after the sample was cooled to RT.

2.3.2. EtPy Adsorption in Different Gas Flows. The sample was put into a stainless steel IR cell with ZnSe windows. Before the adsorption of EtPy, the solid sample was treated in gas flow (50 cm³/min) according to the following procedure: H₂ (T = 673 K, t = 120 min) → Ar (T = 723 K, t = 60 min) → Ar (T = 300 K). EtPy was introduced onto the sample in Ar or H₂ flow by passing through an EtPy-containing bubble tank and then to the IR cell. The amount of EtPy introduced into the IR cell can be controlled by the bubbling time. After the cell was purged for 30 min with Ar or H₂, the IR spectrum was recorded. For the experiment of EtPy adsorption on H₂ preadsorbed Pt/ γ -Al₂O₃ in Ar flow, EtPy was introduced in Ar flow onto Pt/Al₂O₃ which was pre-equilibrated with H₂ for 3 min.

2.3.3. EtPy Adsorption on Pt/ γ -Al₂O₃ Premodified with Cinchonidine (CD). After activating in H₂ at 673 K for 120 min, 0.1 g of 5% Pt/ γ -Al₂O₃ was immersed in 10 mL of 0.001 M CD/ethanol solution and stirred for 10 h to obtain the CD-premodified Pt/ γ -Al₂O₃. Then the CD-premodified Pt/ γ -Al₂O₃ was transferred to an in-situ diffuse reflectance IR cell under the protection of Ar (special care was taken to close the IR cell immediately to isolate the samples from air before solvent evaporation). The cell was purged with Ar to evaporate the solvent ethanol on samples at 353 K for 1 h and then cooled to 300 K. EtPy was introduced onto CD-Pt/ γ -Al₂O₃ in Ar or H₂

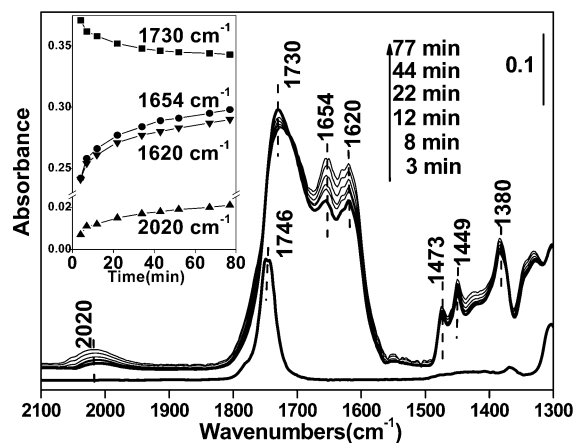


Figure 1. In situ IR spectra collected at different times after admission of 0.5 Torr EtPy onto Pt/ γ -Al₂O₃. The bottom line is the IR spectrum of gas-phase EtPy (at ca. 3 Torr, 10 cm optical path). The inset shows the variation of IR band intensity with the adsorption time. T = 300 K.

stream for several seconds. After the cell was purged for 30 min with Ar or H₂, IR spectra were recorded.

3. Results and Discussion

3.1. EtPy Adsorption in Vacuum. Figure 1 displays the IR spectra of free EtPy molecules in the gas phase and adsorbed EtPy on Pt/ γ -Al₂O₃. Free EtPy molecules show no IR absorption in the region of 1700–1500 cm⁻¹ and a dominant IR band at 1746 cm⁻¹ due to the vibration of C=O groups in EtPy. EtPy molecules form hydrogen bonds with surface hydroxyl groups of γ -Al₂O₃, resulting in the decline of band intensity at 1746 (isolated Al–OH), 1732 (bridged OH), and 1687 (multicentered OH) cm⁻¹ and the increase of the broadband centered at 3550 cm⁻¹ (not shown). The IR spectra of free and adsorbed EtPy both show bands at 1473, 1449, and 1380 cm⁻¹. The bands at 1730, 1620, and 1654 cm⁻¹ dominate the IR spectra of adsorbed EtPy on Pt/ γ -Al₂O₃. A comparison of the IR spectra of free and adsorbed EtPy demonstrates that the two prominent bands at 1620 and 1654 cm⁻¹ are not due to simply adsorbed EtPy. A band appears at 2020 cm⁻¹ due to linearly adsorbed CO on Pt of Pt/ γ -Al₂O₃. The band intensities at 1620, 1654, and 2020 cm⁻¹ increase along with adsorption time accompanied by the decline of the band intensity at 1730 cm⁻¹. The inset of Figure 1 shows that the intensities of some IR bands change with the adsorption time. The variation of band intensities with time suggests that some chemical reactions take place along with the EtPy adsorption on Pt/Al₂O₃ even at RT. The appearance of adsorbed CO indicates that EtPy decomposes on Pt/ γ -Al₂O₃ and the CO and other fragments are formed.^{20,21} It is not yet clear whether the bands at 1654 and 1620 cm⁻¹ are from the same type of species, though they change in similar trends.

Adsorbed EtPy on γ -Al₂O₃ (Figure 2) also show very different IR bands from those of free EtPy. Bands at 1654, 1619, and 1727 cm⁻¹ with a shoulder at 1760 cm⁻¹ dominate the IR spectra of adsorbed EtPy on Al₂O₃. The band intensities at 1654, 1619, and 1760 cm⁻¹ increase with adsorption time accompanied by the decline of the band intensity at 1727 cm⁻¹. The similar IR characteristics of adsorbed EtPy on Pt/ γ -Al₂O₃ and γ -Al₂O₃ indicate that most of the EtPy molecules are adsorbed on γ -Al₂O₃. The bands at ca. 1730 cm⁻¹ can be attributed to C=O vibrations in adsorbed EtPy molecules H-bonded to hydroxyl groups or coordinated to unsaturated Al³⁺ sites on γ -Al₂O₃.²⁸ The appearance and variation of IR bands at 1654, 1619, and

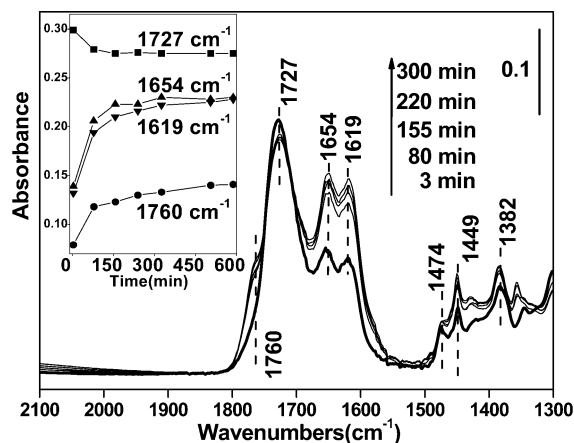


Figure 2. In situ IR spectra collected at different times after admission of 0.5 Torr EtPy onto γ -Al₂O₃. The inset shows the variation of IR band intensity with the time. $T = 300$ K.

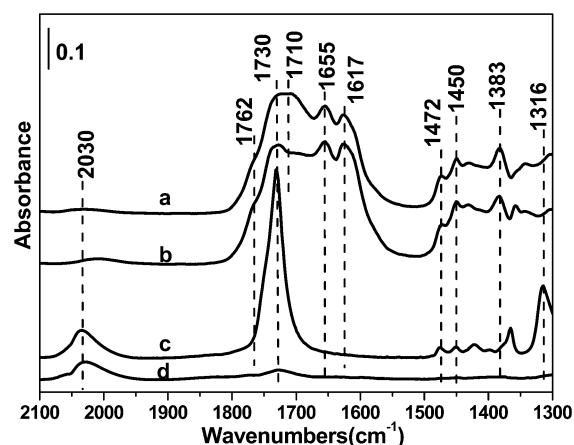


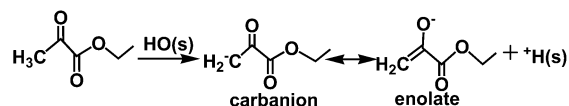
Figure 3. In situ IR spectra collected after admission of 0.5 Torr EtPy onto (a) Pt/ γ -Al₂O₃ and (c) Pt/SiO₂ after closed IR cell for 10 h at 300 K. After subsequent degassing at 373 K for 40 min, IR spectra of adsorbed EtPy on (b) Pt/ γ -Al₂O₃ and (d) Pt/SiO₂ were recorded.

1760 cm⁻¹ are due to some species formed from the reactions of EtPy on Al₂O₃.

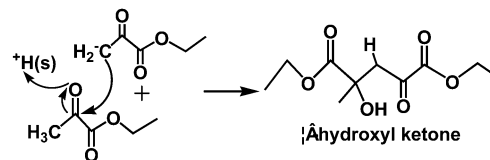
Figure 3 shows the adsorption and desorption of EtPy on Pt/ γ -Al₂O₃ and Pt/SiO₂. IR bands due to linearly adsorbed CO on Pt appear in the region of 2100–2000 cm⁻¹ on the two catalysts. The IR spectrum of EtPy on Pt/SiO₂ shows a negative band at 3734 cm⁻¹ and a broadband centered at 3400 cm⁻¹ in the high-frequency region (not shown). This indicates that some EtPy molecules interact with surface hydroxyls on SiO₂. Adsorbed EtPy molecules on Pt/SiO₂ show no IR bands in the region of 1700–1500 cm⁻¹. Comparison with IR spectra of EtPy on Pt/SiO₂ confirms that IR bands at 1655, 1620, and 1760 cm⁻¹ on Pt/ γ -Al₂O₃ result from the interaction between EtPy and Al₂O₃. When the system was degassed at 373 K, the IR bands of the adsorbed EtPy on Pt/SiO₂ are greatly attenuated, while the spectrum of the adsorbed EtPy on Pt/ γ -Al₂O₃ is nearly unchanged. This indicates that γ -Al₂O₃ has stronger adsorption abilities than SiO₂ for EtPy and the species from the reactions of EtPy. The terminal OH groups on Al₂O₃ have basic character as compared to the bridging and multicentered OH groups.^{26,27} Sufficient evidence was provided for the availability of coordinatively unsaturated tetrahedral and octahedral Al³⁺ sites with Lewis acidity on γ -alumina surfaces.²⁹ Both hydroxyl groups and unsaturated Al³⁺ sites on γ -Al₂O₃ could bond with carbonyl groups of EtPy. While on SiO₂, EtPy molecules are weakly H-bonded to surface hydroxyl groups.

SCHEME 1: Proposed Mechanism for Aldol Condensation of EtPy Catalyzed by the Base–Acid Sites on the γ -Al₂O₃ Surface

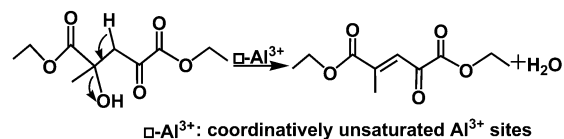
(1) Keto to carbanion (enolic form) conversion:



(2) Addition reaction:



(3) Dehydration reaction:



Ferri et al. proposed that EtPy can undergo alumina-catalyzed hydrolysis and aldol type condensation in H₂ saturated CH₂-Cl₂.²⁴ Pyruvic acid from EtPy hydrolysis on the Al₂O₃ surface results in IR absorption of carboxylates at ca. 1620 cm⁻¹ ($\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$). Aldol condensation of adsorbed EtPy on γ -Al₂O₃ leads to the formation of (C=O)- and (C=C)-containing species, which are associated with the signals at 1732 and 1645 cm⁻¹.²⁴ We agree with their suggestion and the assignment of the IR bands. Here, we assign IR bands at 1617 cm⁻¹ to the carboxylates species derived from the hydrolysis of EtPy on γ -Al₂O₃ and 1655 cm⁻¹ to (C=C)-containing species formed from the aldol condensation of EtPy catalyzed by γ -Al₂O₃. In the experiments performed by Ferri et al., an IR band at 1760 cm⁻¹ was not observed. The IR band at 1760 cm⁻¹ with a frequency higher than the vibrations of C=O bonds in EtPy (1746 cm⁻¹) could be assigned to the species with C=O bonds which are not conjugated with other C=C and C=O bonds in the products of aldol condensation of EtPy on γ -Al₂O₃. Although the quantitative kinetics results are difficult to obtain only from IR spectra, all the side reactions on Pt and alumina are on the order of several minutes as shown in Figure 1.

From an organic chemistry point of view, a proton can be removed from a ketone by a base (OH⁻) catalyst to give a carbanion (enolic form), which then adds to the carbonyl double bond, yielding β -hydroxyl ketone. The dehydration of β -hydroxyl ketone gives α,β -unsaturated ketone catalyzed by acid or at higher temperature. This reaction is the so-called aldol condensation. It has been well characterized that acid–base pair sites are present on alumina.³⁰ The acid–base sites on alumina facilitate acetone chemisorption and activation for aldol condensation reactions on surface, leading to the formation of mesityl oxide species ((CH₃)₂C=CHCOCH₃). More availability of Brønsted acid sites on silica–alumina enhances the surface reactions.²⁸ In the absence of acid–base sites, acetone molecules are weakly H-bonded to surface hydroxyl groups without any further surface reactions.²⁸ We suggest that base–acid sites on the γ -Al₂O₃ surface are responsible for the aldol reaction of EtPy to yield β -hydroxyl ketone, which is subsequently dehydrated to generate C=C-containing species (as shown in Scheme 1). The fact that the aldol condensation of EtPy on Al₂O₃ could be suppressed by adsorbed acetic acid²⁴ may be interpreted as that the acetic acid can adsorb and block some basic sites on alumina. The inability of SiO₂ surface to

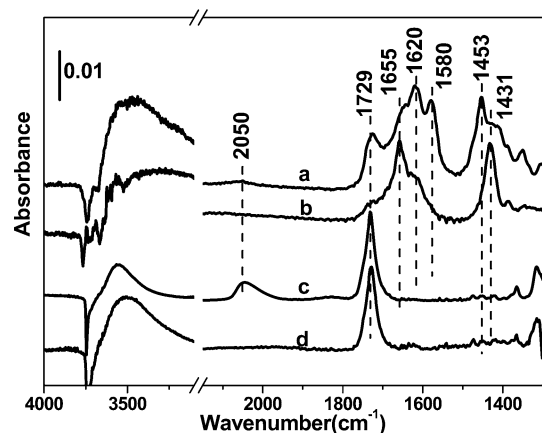


Figure 4. In situ IR spectra recorded after introducing EtPy onto (a) Pt/ γ -Al₂O₃, (b) γ -Al₂O₃, (c) Pt/SiO₂, and (d) SiO₂ in Ar gas flow. $T = 300$ K.

chemisorb and activate EtPy molecules stresses the necessity of acid–base sites for the side reactions.

3.2. EtPy Adsorption in Ar Atmosphere. A great amount of EtPy is adsorbed on samples in the vacuum adsorption experiments, as indicated by the strong IR bands in Figure 1–3. Murzin et al. showed that, in heterogeneous hydrogenation of ethyl pyruvate, ligand acceleration could be observed at a higher concentration of EtPy, whereas at lower concentration, both enantioselective and racemic reactions have very similar reaction rates.¹⁰ Adsorption of a relatively small amount of EtPy on Pt catalysts should also be studied by IR spectroscopy. Experiments were done in gas flow by passing through an EtPy-containing bubble tank then to an IR cell. The amount of EtPy introduced into the IR cell can be controlled by the bubbling time.

Introducing EtPy for several minutes by Ar flow results in strong IR bands of adsorbed EtPy on Pt/ γ -Al₂O₃ (not shown) similar to Figure 1. The IR band at 2050 cm⁻¹ of linear CO adsorption on Pt of Pt/ γ -Al₂O₃ emerges and shifts to 2020 cm⁻¹ along with increasing the adsorption amount of EtPy.

By reducing the quantity of EtPy adsorbed on the catalyst, EtPy was introduced into the IR cell by Ar stream for 15 s. IR spectra of adsorbed EtPy on four selected catalysts were recorded and shown in Figure 4. The IR band at 2050 cm⁻¹ of adsorbed CO due to EtPy decomposition on Pt can be observed in the presence of Pt. The IR spectrum of a relatively small amount of EtPy adsorbed on γ -Al₂O₃ (Figure 4b) shows the predominant IR bands at 1660, 1620, and 1431 cm⁻¹. The characters of IR spectra are not affected by the adsorption amount of EtPy on Pt/SiO₂ (Figure 3c and Figure 4c) and showed prominent bands at ca. 1730 and 2050 cm⁻¹. The band at 1580 cm⁻¹ becomes apparent (Figure 4a and Figure 1), when the amount of EtPy adsorbed on Pt/ γ -Al₂O₃ is reduced. Owing to the fact that the IR bands at 1580 and 1452 cm⁻¹ can hardly be detected for Pt/SiO₂ and γ -Al₂O₃, we assumed that the decomposition products of EtPy on Pt could interact with Al₂O₃ to generate some species, which give these two bands. The IR results showed that the formation of carboxy and formate species occurred at the CO/Al₂O₃ and CO/ZrO₂ interfaces.^{31,48} The two bands at 1580 and 1452 cm⁻¹ may be attributed, respectively, to antisymmetric and symmetric $\nu(\text{OCO})$ vibrations of formate species adsorbed on alumina.^{32–34} It is proposed that CO formed from EtPy decomposition on Pt then reacts with hydroxyls on alumina to generate a small quantity of formate species. When a great amount of EtPy is adsorbed on Pt/ γ -Al₂O₃, most of the hydroxyls on Al₂O₃ are H-bonded with EtPy and then little hydroxyls are left to interact with CO, so that IR band at 1580 cm⁻¹ is indiscernible in Figure 1.

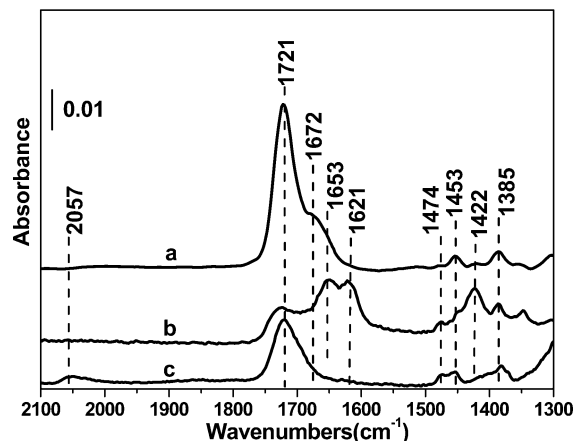


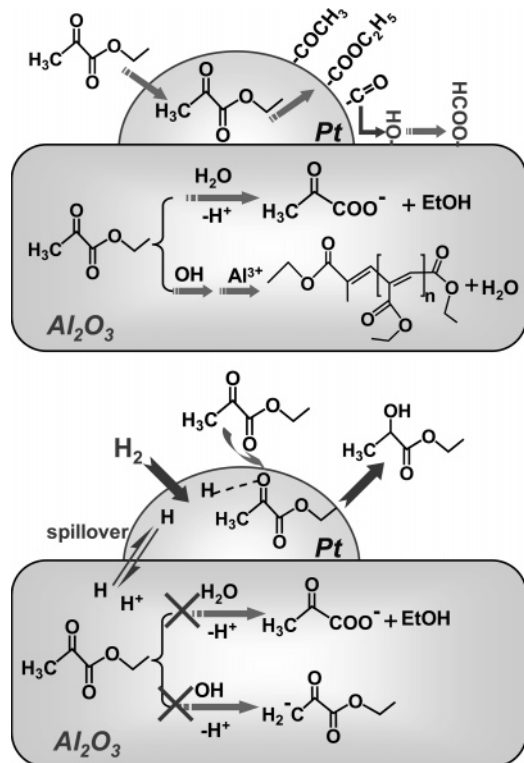
Figure 5. In situ IR spectra recorded after introducing EtPy onto (a) Pt/ γ -Al₂O₃, (b) γ -Al₂O₃, and (c) Pt/SiO₂ in H₂ gas flow. $T = 300$ K.

3.3. EtPy Adsorption in H₂ Stream. Several different side reactions of adsorbed EtPy have been observed in the absence of H₂ and solvent. Side reactions of EtPy on Pt and adjacent γ -Al₂O₃ lead to the blocking of the active sites on Pt surface with fragmentation and polymerization products. Catalyst deactivation has been observed in kinetic experiments.^{10,16} In H₂-saturated CH₂Cl₂, addition of acetic acid was found to suppress the aldol condensation and hydrolysis of EtPy on γ -Al₂O₃.²⁴ In fact, high enantioselectivity and conversion can be obtained in the absence of acidic solvent (such as ethanol, CH₂Cl₂, and toluene or in the absence of solvent⁴⁷). It is very important to identify which species accounts for suppressing side reactions of adsorbed EtPy in the absence of acidic solvent. The effect of other components of the reaction system on EtPy adsorption and reaction should be investigated.

Controlling introduction time for 15 s, IR spectra of adsorbed EtPy (Figure 5) were recorded in H₂ flow after 30 min. Figure 5 clearly shows that the presence of H₂ gas has a significant influence on IR spectra of adsorbed EtPy in comparison with those in Ar (Figure 4). For Pt/SiO₂, the band due to C=O vibration of adsorbed EtPy shifts from 1729 cm⁻¹ in Ar (Figure 4c) to 1721 cm⁻¹ in H₂ (Figure 5c) and becomes broader. The dissociative adsorption of H₂ on Pt may increase the electron density of the Pt surface^{35–37} and affect the adsorption state of EtPy, as indicated by the fact that the $\nu(\text{C=O})$ of adsorbed EtPy shifts to lower frequency in the presence of H₂. Scanning tunneling microscopy (STM) results showed that, in the presence of H atoms, EtPy distributed uniformly on Pt{111} surface.⁸ Another interpretation for the shift of $\nu(\text{C=O})$ may be due to the formation of H-bonds between C=O groups of EtPy and H atoms on Pt. The formation of this type of H-bond is proposed to be possibly the first step of the hydrogenation reaction.

Figure 5a shows the IR spectrum recorded after Pt/ γ -Al₂O₃ was exposed to EtPy in H₂ flow. A prominent band at 1721 cm⁻¹ and the shoulder bands at 1672 and 1653 cm⁻¹ are observed, while IR bands at 1620 and 1580 cm⁻¹ observed in Ar flow (Figure 4a) can hardly be detected in the presence of H₂ (Figure 5a). However, for γ -Al₂O₃ alone (Figure 5b), the bands at 1653 and 1620 cm⁻¹ are still observed. It is apparent that the presence of H₂ can significantly suppress the decomposition and aldol condensation of adsorbed EtPy on Pt/ γ -Al₂O₃. The hydrolysis of EtPy on Pt/ γ -Al₂O₃ is thoroughly inhibited by the presence of H₂. On γ -Al₂O₃ alone, aldol-type condensation and hydrolysis of EtPy still occur in H₂ flow.

It is generally believed that H atoms formed on Pt could spill over to the γ -Al₂O₃ surface.^{35–37} It is unambiguous that H atoms are the species inhibiting side reactions of adsorbed EtPy on

SCHEME 2: Proposed Mechanism for the Side Reactions of EtPy on Pt/Al₂O₃ Inhibited by H₂

the γ -Al₂O₃ surface. In the absence of Pt, the inability of H₂ to inhibit side reactions of adsorbed EtPy confirms the beneficial function of spilt-over H atoms. Transient kinetic experiments showed that lowest initial rates (for asymmetric hydrogenation) were measured with simultaneous introduction of all reaction components prior to that of hydrogen.¹⁶ In ref 16, this behavior is attributed to undesired side reactions of EtPy and the cinchonidine occurring in the liquid phase. In fact, the lowest initial rate was the racemic hydrogenation of EtPy, where EtPy contacted with Pt/Al₂O₃ first then H₂ introduced.¹⁶ Side reactions occur on both the Pt and the alumina support and lead to blocking of the active platinum surface by fragmentation and polymerization products.²⁴ Ferri et al. showed that addition of acetic acid was found to suppress the aldol condensation and hydrolysis of EtPy on Pt/ γ -Al₂O₃.²⁴ For the first time, our IR results give the observations and proof that spilt-over hydrogen from Pt to alumina can suppress the acid–base activity of alumina for EtPy side reactions and facilitate the hydrogenation reaction.

A series of experiments was designed to study the effect of substrate quantity on the side reactions and verify the role of spilt-over hydrogen in the reaction. Increasing the quantity of adsorbed EtPy, DRIFTS spectra (Figure 6) were collected for γ -Al₂O₃, Pt/ γ -Al₂O₃, Pt/SiO₂ + γ -Al₂O₃ (1:1 wt) mixture, and Pt/ γ -Al₂O₃ + γ -Al₂O₃ (1:1 wt.) mixture. For γ -Al₂O₃, IR bands at 1767, 1730, 1655, and 1620 cm⁻¹ can be observed clearly (Figure 6a) in H₂ flow. The IR spectra of adsorbed EtPy in the presence of H₂ have similar characters for the Pt/SiO₂ + γ -Al₂O₃ (1:1 wt) mixture, Pt/ γ -Al₂O₃ + γ -Al₂O₃ (1:1 wt) mixture, and Pt/ γ -Al₂O₃ (parts b, c, and d of Figure 6). The bands at 1997, 1767, and 1620 cm⁻¹ are hardly detected, and the band at 1655 cm⁻¹ is greatly attenuated. When purged with Ar flow for 60 min after Figure 6d, the bands at 1997, 1655, and 1620 cm⁻¹ rise to some extent as shown in Figure 6e. For Pt/ γ -Al₂O₃ pre-equilibrated with H₂ (Figure 6f), the bands at 1997, 1655, and 1620 cm⁻¹ due to the products from surface side reactions of

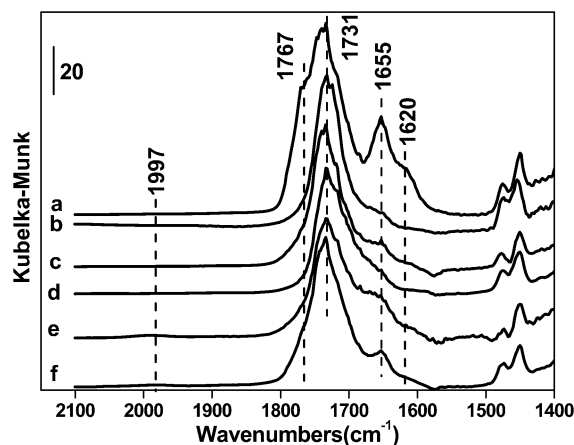


Figure 6. In situ DRIFT spectra of adsorbed EtPy in H₂ gas flow on the following: (a) γ -Al₂O₃, (b) Pt/SiO₂ + γ -Al₂O₃ (1:1 wt), (c) Pt/ γ -Al₂O₃ + γ -Al₂O₃ (1:1 wt), and (d) Pt/ γ -Al₂O₃. Spectrum e is obtained after changing to Ar flow for 60 min after d. Spectrum f corresponds to adsorbed EtPy in Ar flow on H₂ preadsorbed Pt/ γ -Al₂O₃. *T* = 300 K.

EtPy are detected with medium intensities compared with parts a and d of Figure 6. The IR spectra of adsorbed EtPy on the former four samples clearly show that the side reactions can be suppressed by the coexistence of Pt and H₂, though the amount of adsorbed EtPy is great. In the two cases where some Al₂O₃ does not contact with Pt (parts b and c of Figure 6), the hydrogen atoms on Pt migrate across the boundaries to suppress the side reactions on Al₂O₃. The decomposition of EtPy on Pt and condensation and hydrolysis on Al₂O₃ all increase to a bigger degree in parts e and f of Figure 6 than in Figure 6d.

Though purging in Ar at room temperature cannot make H atoms desorb from γ -Al₂O₃ directly, some H atoms on γ -Al₂O₃ can spillover back and desorb from Pt.⁴⁴ Our IR results (Figure 6) show that abundant H atoms are necessary to inhibit the side reactions of EtPy on Pt/ γ -Al₂O₃ surface. In the ATR-IR experiments of Ferri et al. where H₂-saturated CH₂Cl₂ was used as the solvent, aldol-type condensation and hydrolysis of EtPy were observed on Pt/Al₂O₃.²⁴ The reason may be that the amount of H₂ dissolved in CH₂Cl₂ under 1 atm is insufficient to inhibit the surface side reactions. In this work, 1 atm H₂ gas was used, so the concentration of H₂ on Pt surface should be higher than that in H₂-saturated CH₂Cl₂. Abundant spilt-over hydrogen atoms are present to suppress side reactions of adsorbed EtPy on Pt/ γ -Al₂O₃. It is supposed that the aldol condensation of EtPy on Pt/ γ -Al₂O₃ can be thoroughly avoided by higher pressure H₂ or high concentration of H atoms on γ -Al₂O₃.

It has been demonstrated that the physical nature of the spilt-over hydrogen, especially their charge, can only be described by considering their interaction with the solid.⁴⁴ H⁺ ions and H atoms coexist on the surface of the catalyst as also proved experimentally. Their ratio is determined by the electronic properties of the adsorbate/solid system. The presence of H⁺ spilt-over species is supported by catalytic reaction tests and studies of the H–D exchange of zeolitic hydroxyls under the influence of a magnetic field at ambient temperature.⁴⁵ We supposed that there are two possible reasons for spillover hydrogen to suppress the surface reactions catalyzed by γ -Al₂O₃ and they are as follows: (1) nucleophilic OH groups (basic) on the surface interact with H⁺ or H atoms, then its acidic–basic property and catalytic activity altered;⁴⁹ (2) the balance of the first step in the aldol condensation of EtPy, removal of a proton

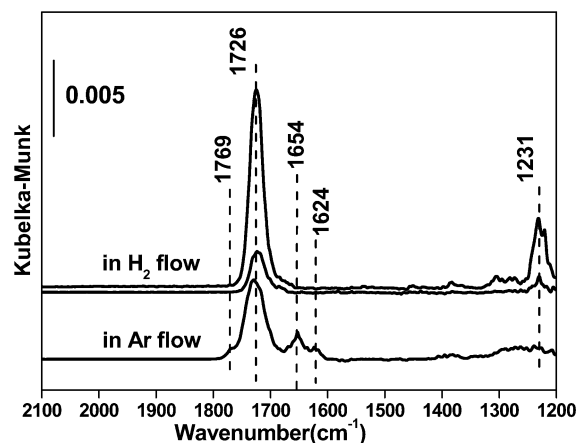


Figure 7. In situ DRIFT spectra of adsorbed EtPy on Pt/ γ -Al₂O₃ premodified with cinchonidine. $T = 300$ K.

from the ketone to give a carbanion, is influenced by the existence of H⁺, as also for the hydrolysis process of EtPy. The proposed mechanism for the inhibition of side reactions of EtPy on Pt/Al₂O₃ by H₂ is shown in Scheme 2.

3.4. EtPy Adsorption on Pt/ γ -Al₂O₃ Premodified with Cinchonidine (CD). Acetic acid can prevent the chiral modifier from adsorbing on Al₂O₃, but the adsorption of CD on γ -Al₂O₃ is inevitable in neutral media.⁴⁶ Using ethanol as solvent makes sure that CD adsorbs not only on Pt but also on γ -Al₂O₃. Figure 7 shows the spectra of adsorbed EtPy on CD-premodified Pt/ γ -Al₂O₃ in Ar and H₂. In Ar flow, the IR spectrum of adsorbed EtPy on CD-Pt/ γ -Al₂O₃ shows four distinct bands at 1769, 1726, 1654, and 1624 cm⁻¹ in the 2100–1200 cm⁻¹ range. When EtPy adsorbed on CD-Pt/ γ -Al₂O₃ in H₂ flow, only two bands at 1726 and 1231 cm⁻¹ can be seen. Decomposition of EtPy does not occur on CD-preadsorbed Pt. But the presence of CD alone cannot inhibit the hydrolysis and aldol condensation of EtPy on γ -Al₂O₃. The coexistence of H₂ and cinchonidine on Pt/ γ -Al₂O₃, thoroughly inhibits the occurrence of aldol condensation and hydrolysis of EtPy.

At the present moment, it is not very clear how the adsorbed CD helps spillover H atoms to suppress the side reaction on Pt and γ -Al₂O₃. It may be that adsorbed CD can promote the dissociation of H₂ on Pt or improve the migration and distribution of hydrogen on Pt/Al₂O₃. The adsorption of CD through the quinoline ring on Pt can change the electronic state of the Pt surface,¹¹ which may increase the ability of Pt for H₂ dissociation at room temperature. The proton movement is water assisted by a vehicle mechanism (hydrogen migration as H₃O⁺ species).⁵⁰ Adsorbed CD molecules may assist the spillover of hydrogen from Pt to γ -Al₂O₃ by coordination with spillover protonic H⁺ through the quinuclidine N in CD. Further studies are needed to get the reason for CD's "helping" role.

The rate acceleration effect induced by the addition of CD has been suggested to be due to its activation ability of α -ketoester through the formation of adsorbed 1:1 complexes on Pt surface, either between the α -ketoester and the protonated modifier or between half-hydrogenated EtPy and the modifier.^{5,9,11,38–43} The fragmentation and polymerization products from side reactions of EtPy on Pt and adjacent γ -Al₂O₃ lead to the blocking of the active sites on the Pt surface.²⁴ Ligand acceleration could be observed at a higher concentration of EtPy, whereas at lower concentration, both enantioselective and racemic reactions have very similar reaction rates.¹⁰ Combined with other literatures, Murzin et al. proposed that cinchonidine can prevent the side reactions of EtPy on Pt/Al₂O₃.¹⁰ However, the IR results presented in this work clearly show that cin-

chonidine alone cannot suppress side reactions of EtPy. Cinchonidine can "help" hydrogen to thoroughly suppress all the side reactions on Pt and alumina surfaces. Our results correct the proposal of Murzin et al. and are consistent with their results to some degree. The IR results lead us to understand more clearly the function of CD and H₂ in enantioselective hydrogenation.

4. Conclusions

The side reactions of EtPy on Pt/ γ -Al₂O₃, including decomposition on Pt, aldol condensation, and hydrolysis on γ -Al₂O₃, respectively, have been investigated in the absence of solvent. CO derived from EtPy decomposition on Pt reacts with the hydroxyl groups of Al₂O₃ resulting in the formation of formate species on the Al₂O₃ surface. It is very interesting to find out that H₂ not only acts as a reactant for hydrogenation reaction but also plays an important role in suppressing the side reactions of EtPy on supported Pt catalysts. It is also found that cinchonidine alone adsorbed on Pt/ γ -Al₂O₃ cannot suppress the aldol condensation and hydrolysis of EtPy on γ -Al₂O₃, and only the coexistence of CD and H₂ can thoroughly inhibit all the side reactions of EtPy on Pt/ γ -Al₂O₃. It is shown that spillover H atoms from H₂ dissociation on Pt account for inhibiting the side reactions on γ -Al₂O₃. Adsorbed CD can assist H₂ in avoiding site-blocking with fragmentation and polymerization products then facilitate hydrogenation on Pt, which may be a reason for the rate acceleration effect of CD. IR studies clarify the roles of H₂ and CD played in suppressing side reactions of EtPy on Pt/ γ -Al₂O₃.

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References and Notes

- (1) Collins, A. N.; Sheldrake, G. N.; Crosby, J. *Chirality in Industry: The Commercial Manufacture and Applications of Optically Active Compounds*; Wiley: New York, 1995.
- (2) Noyori, R. *CHEMTECH* **1992**, 22, 366.
- (3) Jannes, G.; Dubois, V. *Chiral Reactions in Heterogeneous Catalysis*; Plenum Press: New York, 1995.
- (4) Blaser, H. U.; Baiker, A. *Handbook of Heterogeneous Catalysis*; VCH Publishers: Weinheim, Germany, 1997; Vol. 5, p 2422.
- (5) Baiker, A. *J. Mol. Catal. A: Chem.* **1997**, 115, 473.
- (6) Blaser, H. U.; Jallet, H. P.; Muller, M.; Studer, M. *Catal. Today* **1997**, 37, 441.
- (7) Wells, P. B.; Wilkinson, A. G. *Top. Catal.* **1998**, 5, 39.
- (8) Bonello, J. M.; Lambert, R. M.; Kunzle, N.; Baiker, A. *J. Am. Chem. Soc.* **2000**, 122, 9864.
- (9) Orito, Y.; Imai, S.; Niwa, S. *J. Chem. Soc. Jpn.* **1979**, 1118.
- (10) Toukoniitty, E.; Murzin, D. Y. *J. Catal.* **2006**, 241, 96.
- (11) Vargas, A.; Ferri, D.; Baiker, A. *J. Catal.* **2005**, 236, 1.
- (12) Studer, M.; Blaser, H. U.; Exnerb, C. *Adv. Synth. Catal.* **2003**, 345, 45, and references cited therein.
- (13) Blaser, H. U.; Jallet, H. P.; Lottenbach, W.; Studer, M. *J. Am. Chem. Soc.* **2000**, 122, 12675.
- (14) Griffiths, S. P.; Johnston, P.; Wells, P. B. *Appl. Catal., A* **2000**, 191, 193.
- (15) Zuo, X.; Liu, H.; Liu, M. *Tetrahedron Lett.* **1998**, 39, 1941.
- (16) Margitfalvi, J. L.; Minder, B.; Talas, E.; Botz, L.; Baiker, A. *Stud. Surf. Sci. Catal.* **1993**, 75, 2471.
- (17) Ferri, D.; Burgi, T.; Borszeky, K.; Mallat, T.; Baiker, A. *J. Catal.* **2000**, 193, 139.
- (18) Wells, R. P. K.; McGuire, N. R.; Li, X.; Jenkins, R. L.; Collier, P. J.; Whyman, R.; Hutchings, G. J. *J. Phys. Chem. Chem. Phys.* **2002**, 4, 2839.
- (19) Bonello, J. M.; Williams, F. J.; Santra, A. K.; Lambert, R. M. *J. Phys. Chem. B* **2000**, 104, 9696.
- (20) Mallat, T.; Bodnar, Z.; Minder, B.; Borszeky, K.; Baiker, A. *J. Catal.* **1997**, 168, 183.
- (21) Ferri, D.; Burgi, T.; Baiker, A. *J. Phys. Chem. B* **2004**, 108, 14384.
- (22) Castonguay, M.; Roy, J. R.; Lavoie, S.; Laliberté, M. A.; McBreen, P. H. *J. Phys. Chem. B* **2004**, 108, 4134.

- (23) Castonguay, M.; Roy, J. R.; Lavoie, S.; Adnot, A.; McBreen, P. *H. J. Am. Chem. Soc.* **2001**, *123*, 6429.
- (24) Ferri, D.; Diezi, S.; Maciejewski, M.; Baiker, A. *Appl. Catal., A* **2006**, *297*, 165.
- (25) Li, X.; You, X.; Ying, P.; Xiao, J.; Li, C. *Top. Catal.* **2003**, *25*, 63.
- (26) Zaki, M. I.; Knözinger, H. *Mater. Chem. Phys.* **1987**, *17*, 201.
- (27) Knözinger, H.; Ratnasamy, P. *Catal. Rev.-Sci. Eng.* **1978**, *17*, 31.
- (28) Zaki, M. I.; Hasan, M. A.; Al-Sagheer, F. A.; Pasupulety, L. *Langmuir* **2000**, *16*, 430.
- (29) Zaki, M. I.; Knözinger, H. *Spectrochim. Acta, Part A* **1987**, *43*, 1455.
- (30) Zaki, M. I.; Hasan, M. A.; Al-Sagheer, F. A.; Pasupulety, L. *Colloid Surf.* **2001**, *190*, 261.
- (31) Iordan, A.; Zaki, M. I.; Kappenstein, C. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2502.
- (32) Kantschewa, M.; Albano, E. V.; Ertl, G.; Knozinger, H. *Appl. Catal.* **1983**, *8*, 71.
- (33) Busca, G.; Lorenzelli, V. *Mater. Chem.* **1982**, *7*, 89.
- (34) Morterra, C.; Zecchina, A.; Coluccia, S.; Chiorino, A. *J. Chem. Soc., Faraday Trans. I* **1977**, *73*, 1544.
- (35) Connor, W. C.; Pajonk, G. M.; Teichner, J. J. *Adv. Catal.* **1986**, *34*, 34.
- (36) Ekstrom, A.; Batley, G. E.; Johnson, D. A. *J. Catal.* **1974**, *34*, 106.
- (37) Parera, J. M.; Traffano, E. M.; Musso, J. C.; Pieck, C. L. *In Spillover of Adsorbed Species*; Pajonk, G. M., Teichner, S. J., Germain, J. E., Eds.; Elsevier: Amsterdam, The Netherlands, 1983; p 101.
- (38) Li, X.; Wells, R. P. K.; Wells, P. B.; Hutchings, G. J. *J. Catal.* **2004**, *221*, 653.
- (39) Balazsik, K.; Bartok, M. *J. Catal.* **2004**, *224*, 463.
- (40) Ma, Z.; Lee, I.; Kubota, J.; Zaera, F. *J. Mol. Catal. A: Chem.* **2004**, *216*, 199.
- (41) Bartok, M.; Sutyinski, M.; Felfoldi, K. *J. Catal.* **2003**, *220*, 207.
- (42) LeBlanc, R. J.; Chu, W.; Williams, C. T. *J. Mol. Catal. A: Chem.* **2004**, *212*, 277.
- (43) Vayner, G.; Houk, K. N.; Sun, Y. K. *J. Am. Chem. Soc.* **2004**, *126*, 199.
- (44) Roland, U.; Braunschweig, T.; Reossner, F. *J. Mol. Catal. A: Chem.* **1997**, *127*, 61.
- (45) Roland, U.; Winkler, H.; Bauch, H.; Steinberg, K. H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3921.
- (46) Toukoniitty, E.; Arvela, P. M.; Kumar, N.; Salmi, T.; Murzin, D. *Y. Catal. Lett.* **2004**, *95*, 179.
- (47) Arx, M.; Dummer, N.; Willock, D. J.; Taylor, S. H.; Wells, R. P. K.; Wells, P. B.; Hutchings, G. J. *Chem. Commun.* **2003**, 1926.
- (48) Kondo, J.; Abe, H.; Sakata, Y.; Maruya, K.; Domen, K.; Onishi, T. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 511.
- (49) Ishikawa, H.; Kondo, J.; Domen, K. *J. Phys. Chem. B* **1999**, *103*, 3229.
- (50) Stoica, M.; Caldararu, M.; Ionescu, N. I.; Auroux, A. *Appl. Surf. Sci.* **2000**, *153*, 218.